

A Manual of Chemistry

For Students of Medicine

Luff and Candy

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A MANUAL OF CHEMISTRY

THEORETICAL AND PRACTICAL
INORGANIC AND ORGANIC

ADAPTED TO THE REQUIREMENTS
OF STUDENTS OF MEDICINE

BY

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PREFACE TO THE FOURTH EDITION

IN the preface to the first edition of this manual the author clearly indicated its aim and scope. Since that time the chemistry required from the student of medicine at his first professional examination has been greatly changed, both in extent and in character. He is now expected to acquire in his first year not only a fuller knowledge of the facts of Chemistry, but a clear conception of the fundamental principles of the science. This change is naturally reflected in his text-book, and is responsible for the unusually extensive alterations in the present edition.

It will perhaps be convenient to indicate some of these alterations more precisely. Part I. has been practically re-written, is considerably enlarged, and now forms, it is hoped, a fairly complete introduction to the chief laws and principles of the science. Pains have been taken to explain these as clearly as possible, for experience shows that it is with them, and not with facts, that the student wants help. A teacher is so accustomed to evolve ideas first and find names for them afterwards that he is tempted to forget that the process is reversed by the average student, who learns the names first and the ideas which they represent afterwards.

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Hence any ambiguity or confusion attaching to the names is transferred to the ideas. The use of different names for the same thing, or of the same name for different things, is a serious stumbling-block to the learner and the cause of much mental confusion. A precision which would perhaps be pedantic in a scientific discussion is therefore by no means out of place in an elementary text-book. These considerations explain the somewhat rigid attitude adopted in reference to hydroxides and hydrates, bases and acids, isomers and metamers, etc.

The additions to Part II. include a detailed account of the estimation required by students reading for the 1st M.B. London, or for the D.P.H., of oxygen and carbon dioxide in air, or other gaseous mixture, by absorption.

Some of the students for whom this book is intended may be required to identify any inorganic substance commonly used in medicine, and to test it for *ordinary impurities*. For this reason the account in Part III. of any such substance now includes a short description of the substance and a list of these impurities, for which reference has generally been made to the British Pharmacopœia.

Part IV. has been entirely recast, partly rewritten, and enlarged. The significance of class-groups is now generally recognised, and constitutional formulæ have therefore in most instances replaced the old ones.

Part V. consists entirely of new matter. The

worked problems may be taken fairly to represent those actually met with in examinations at the present time.

Part VI. has also been completely remodelled, and sufficiently widened to meet the analytical requirements of the various examining bodies concerned. Where these differ in minor details—as, for instance, in the inclusion, or otherwise, of such substances as strontium and manganese—the scheme presented indicates the alternative table to be adopted in each particular case.

Throughout the revision of the book the object in view has been to adhere to the original motive and make it a satisfactory working handbook of Chemistry for any student of medicine. Examples of clinical interest or importance are therefore more frequent than they would be in a similar book intended for students in general. It is, however, *especially*, rather than *exclusively*, suited for students of medicine, and is now believed to contain as complete an introduction to the general theory and practice of Chemistry as could usually be compassed by a student of the science in his first year.

H. C. H. C.

May, 1910.

PREFACE TO THE FIRST EDITION

THIS book is intended as a guide to the study of chemical science for the use of students of medicine. Now that Chemistry, and especially Organic Chemistry, has become so vast a science, the student of medicine is, on the one hand, apt to find himself out of his depth in attempting the perusal of the larger hand-books on the subject; and, on the other hand, with many of the smaller works, excellent in their way, he is hampered by omission of matter essential to the successful after-study and practice of medicine. This book has therefore been written to bring together in a concise form those portions of chemical science that directly or indirectly bear on the study and practice of medicine.

To gauge correctly the wants of the student of medicine, and to appreciate rightly the position that must be assigned to the study of Chemistry amongst his multifarious work, can, in my opinion, be best done by one who has himself been through the courses of study and work required for qualifying in medicine. I have therefore undertaken the task of writing this book in the hope that it may supply a long-felt want, and that it may assist the student in acquiring a sound knowledge of the fundamental principles of Chemistry.

A. P. L.

April, 1892.

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MANUAL OF CHEMISTRY

PART I.—INTRODUCTION TO THE STUDY OF CHEMISTRY

CHAPTER I

FORMS OF MATTER—CHEMICAL ATTRACTION

Matter—Solids—Liquids—Gases—Latent Heat—Critical Temperature—Single Substances and Mixtures—Elements and Compounds—Thermal Phenomena of Chemical Action—Exothermic and Endothermic Compounds—Effect of Temperature on Rate of Chemical Action—Nature of Heat—Energy—Conservation of Energy—Difference of Potential—Positive and Negative Elements—Chemical Attraction.

THE Science of Chemistry is one important branch of the Science of Matter. We must therefore at the very commencement of our study of Chemistry endeavour to form clear ideas of what Matter is. The most cursory observation of his environment will convince a student that he is surrounded by visible and tangible objects which differ in many obvious features but possess at least two properties in common. These two properties are familiarly known as **weight** and **extension**. We know of no form of matter that does not possess both. Every lump of matter—or, as we shall generally term it in future, every *mass*—attracts, and is attracted by,

2 INTRODUCTION TO CHEMISTRY [PART I

every other mass in the universe with a certain force. Weight is the name we give to the response of this force, acting between any mass and the earth, when we attempt to overcome it. Extension is the property by virtue of which all matter takes up room in space. In the case of solid or liquid bodies this is sufficiently obvious, and a little consideration will convince us that gaseous bodies also possess extension. A pneumatic tyre, when inflated with air, takes up more room than when not inflated. These two properties, then—weight and extension—belong to all kinds of matter, and nothing that has not these properties will be called matter. A shadow possesses neither, and is therefore “immaterial.”

Although we cannot easily find any other property common to *all* masses, we have no difficulty in finding many which possess at least a third property in common. Indeed, we have already recognised this in our rough classification of them as *solid*, *liquid*, or *gaseous*. These names refer to what is called the **state of aggregation** of matter in the substance. Aggregation means a flocking or crowding together, and has the same root as is found in the Latin word *grex*, *greg-is*, a flock. The word therefore implies a belief that the mass of the substance is a flock or crowd of something, and we do, in fact, believe that every mass we *can* see is composed of a great crowd of smaller masses which we *cannot* see, but nevertheless have named *molecules* or *little masses* (diminutive of *moles*, a mass). We draw the same distinction when we use the terms *molar* and *molecular* to denote phenomena associated respectively with *masses* and *molecules*. It must not be supposed that the molecules are in actual contact with one another in any one of these states of aggregation. They are separated by spaces in

each case. The student will be prepared to infer that this is true of **gases** from the fact that the *same mass* of gas so readily fills any vessel, small or large, in which it is contained. Since the number of molecules remains the same, the simplest explanation of this fact is found in the supposition that they can approach nearer to each other or move farther apart, and therefore that there are spaces between them. That **liquids** have spaces between their molecules may similarly be inferred from the fact that when certain liquids are mixed together a contraction in bulk is observed. If alcohol and water be mixed together, a diminution in volume occurs, the particles getting closer together than they formerly were, due to a molecular combination of the alcohol with the water. Thus, in making proof spirit, 100 fluid ounces of rectified spirit are mixed with 60 fluid ounces of water, yet only 156 fluid ounces of proof spirit result, a contraction of about $2\frac{1}{2}$ per cent. having taken place.

It may seem, however, more difficult to believe that a **solid** piece of platinum foil has not really that smooth continuous structure which it appears to have, but consists of individual molecules separated by spaces. Examined under a good lens, the skin of the hand, or even the edge of a razor, loses its apparent smoothness, and this may prepare the student to believe that surfaces which appear smooth and continuous may in reality have a grained structure. This belief is confirmed by the fact that, when powerfully compressed, solids are found to occupy a smaller bulk than they did previously to being submitted to pressure.

The grained structure of matter may also serve to explain what is technically called the "sweating" of iron in the Bramah hydraulic press, where water under powerful pressure is actually forced through

4 INTRODUCTION TO CHEMISTRY [PART I

the pores of a stout iron cylinder, although to the eye the iron appears perfectly compact and homogeneous.

The student must clearly understand that in classing a substance as a solid, liquid, or gas we are guided by the state of aggregation in which the substance is, *as a rule*, familiar to us. He must not suppose that the substance can *only* exist in that state. For instance, we class *water* as a liquid, though we often see the same substance in the solid state as *ice*, and in the gaseous state as *steam*. We know that the change from one state to the other may be effected, in this case, by the addition or abstraction of heat. For by the application of heat, *ice* at 0° C. is melted and becomes *water* at 0° C., and by the continued application of heat the cold water becomes warmer and warmer till it attains a certain temperature, usually about 100° C., at which it begins to boil—to be converted, in fact, into the gas *steam*; but, although we continue to supply heat, the substance will not get any hotter, till this conversion is complete. The temperature remains constant during ebullition. The heat does not produce its most common effect—rise of temperature, and for that reason was said to disappear and was called by Black **latent heat** (*latens*, *latent-is*, lying hid). Conversely, the steam is condensed to water if heat is abstracted from it, as, for instance, by using it to warm cold vessels on the water baths so much employed in the laboratory. The change from ice to water, or vice versa, is attended by precisely similar thermal phenomena. The temperature of the mixed ice and water, if properly stirred, remains constant while melting continues, the heat supplied becoming “latent”; but this latent heat reappears, and may be recovered, when water freezes.

These phenomena are not peculiar to water. If

a piece of solid roll sulphur be heated in a test-tube or flask, it will first melt to a yellow liquid, and this on further heating will boil away, forming a heavy vapour* of a reddish-brown colour. Now, if part of the heat be abstracted from the sulphur vapour, this will condense to a syrupy fluid; and this fluid on further cooling (that is, on further abstraction of heat) will solidify to a mass of solid sulphur.

The melting-point and boiling-point of iodine are not very widely separated, and if a piece of the solid be heated in a test-tube it seems to be converted almost directly into a violet vapour*; the vapour will quickly revert to the solid state on coming in contact with the upper and colder portion of the test-tube, which deprives it of its latent heat.

These and many similar examples show that—

A change in the state of aggregation of matter is always accompanied by the absorption or evolution of heat. This heat is associated only with the change of state, and produces no change in the temperature of the matter. It is therefore called latent heat.

Critical temperature.—From the classical experiments of Andrews with “carbonic acid” we learn that for each substance there is a certain temperature above which the substance will be a gas, though exposed to the greatest pressure we can command. This temperature is called the **critical temperature** for the substance. It is about 31° C. for *carbonic acid*, but is a great deal *higher* for water, and a

* The term *vapour* is generally used to denote the gaseous form of a substance which, at ordinary temperatures, is solid or liquid; the term *gas* is preferred when the substance is gaseous at ordinary temperatures.

great deal *lower* for hydrogen. The earlier attempts to liquefy hydrogen and the so-called permanent gases failed, mainly because these gases, when exposed to sufficient pressure, were not reduced to a temperature *below their critical points*. Recent experiments have been more successful, not by reason of increased pressure, but by improved methods of obtaining and preserving low temperature.

SINGLE SUBSTANCES—ELEMENTS AND COMPOUNDS—MIXTURES

We shall soon have occasion to consider more fully the nature of heat and its relation to chemical action, but before doing so it will be convenient to carry our classification of matter a little farther by subdividing each of our three main groups into smaller ones. We divide solids, for instance, into—

- (1) **Single substances**, masses which consist of one substance only; and
- (2) **Mixtures**, masses which consist of two or more single substances.

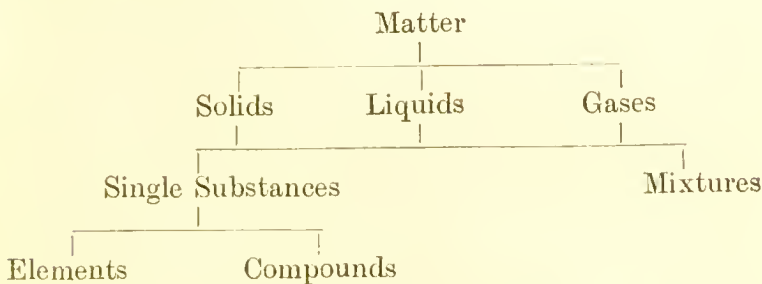
We further divide (1) into—

- i. **Elements**, single substances which can *not* be decomposed into two or more different substances; and
- ii. **Compounds**, single substances which *can* be decomposed into two or more different substances.

The student has already learned that the distinction between solids, liquids, and gases is convenient rather than essential, and that the same substance may often be made to assume any one of the three states. He will therefore be prepared to find that these new subdivisions also extend to liquids and gases.

The classification is, for many reasons, so important that the following diagram is presented to

make the scheme quite clear to the student, as far as we have yet traced it:—



The student must carefully distinguish a **mixture** of two or more constituents from a **compound** of the same. In the *compound* these constituents have combined to form a single new substance with new properties of its own, while the old constituents with their properties have ceased to exist. In the *mixture* these constituents have been more or less intimately mingled, but each constituent continues to exist and to preserve its own individuality; no new substance is formed, and therefore no new property makes its appearance. The constituents also may be *mixed* in any proportions; they can only be *combined* in certain fixed proportions. A good example, often employed to illustrate these distinctions, is supplied by the comparison of a *mixture* of two elements, iron and sulphur, with a *compound* of the same, called iron sulphide.

If iron filings and powdered sulphur be rubbed together, it will be found that the mixture possesses all the properties of its constituents unaltered; for, with a magnet, the iron filings can be picked out and the sulphur left; or, by treating the mixture with a liquid called bisulphide of carbon, the sulphur can be dissolved out and the iron filings left; on evaporating the bisulphide of carbon solution, the sulphur will be left. But if the iron filings and

sulphur be heated in a crucible, chemical combination takes place, and a black mass of sulphide of iron is formed; this chemical compound possesses properties entirely different from those of its constituents. A magnet is now incapable of abstracting the iron from it; bisulphide of carbon will not dissolve out the sulphur from it; on treating it with dilute sulphuric acid, a gas, called sulphuretted hydrogen, possessing an offensive odour, is evolved; neither iron nor sulphur possesses the property alone of evolving this gas when treated with dilute sulphuric acid. As may be readily comprehended, a mixture of iron filings and sulphur could be made with any proportions of the constituents, whereas the chemical compound sulphide of iron requires the constituents to be present in the fixed proportions of 56 parts by weight of iron to 32 parts by weight of sulphur.

EXOTHERMIC AND ENDOTHERMIC COMPOUNDS

Remarkable thermal effects also distinguish the process of combination from one of mere mixture. **The formation of a chemical compound is always attended by the evolution or absorption of heat.**

Exothermic compounds are those at whose formation heat is *evolved*; water and carbon dioxide are common examples of this large class. **Endothermic** compounds are those at whose formation heat is *absorbed*. Hydrogen iodide, ozone, and nitrous oxide ("laughing gas") are examples of this class.

The following are examples of exothermic chemical action:—

If a piece of the metal potassium be thrown upon water, the potassium decomposes the water, forming potassium hydroxide, and evolving part of the

hydrogen of the water; the heat produced by this chemical action is sufficient to set fire to the escaping hydrogen, which burns with a violet-coloured flame (the colour being due to a trace of potassium volatilised by the heat). If a small piece of dry phosphorus be placed on a fragment of iodine, the two substances will immediately commence to combine and form iodide of phosphorus, and the heat, produced by this chemical combination, ignites that portion of the phosphorus which has not already united with the iodine. The lime-light affords another good illustration of heat produced by chemical action. To produce the light, the oxy-hydrogen flame is made to impinge on a piece of lime; the oxygen and hydrogen in combining chemically with each other produce an intense heat, and this raises the particles of the lime, upon which the flame impinges, to a white heat; the particles of lime, glowing at this white heat, emit the dazzling light.

Another, and a still more common, example of heat produced by chemical action is that derived from the burning of coals in our fire-grates. In this case the constituents of the coal combine chemically with the oxygen of the air, the heat resulting from this chemical action causes the coals to glow, and inflames the gases escaping from the burning coal. In fact, in most cases where heat is obtained artificially, it is the result of chemical action.

One last important example of heat produced by chemical action is that of animal heat, or the heat which maintains the temperature of the living body. The oxygen of the air that we inhale is absorbed by the blood circulating through the lungs, and is then conveyed in the blood to the various tissues of the body, where the carbon and hydrogen of the tissues become oxidised, or burnt, by this oxygen to carbonic acid gas and water respectively, and it is the

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heat produced by this chemical action—by this oxidation—which serves to maintain the temperature of the animal body.

The decomposition of a compound being the reversal of its formation, it is naturally attended with *reverse* thermal effects. Accordingly, the disruption of endothermic compounds is attended by the evolution of heat, whereas heat is absorbed in the breaking-down of exothermic combination.

EFFECT OF TEMPERATURE ON THE RATE OF CHEMICAL ACTION

In addition to the particular thermal effects already described, heat exercises a very important influence on chemical action in general. Actions which proceed very slowly at ordinary temperatures—so slowly, perhaps, as to escape observation—proceed more and more rapidly as the temperature rises. It has been estimated that a rise of 10° C. in the temperature quite doubles the rate of many reactions; as a further rise of 10° will again double the rate, we see that the acceleration proceeds in a geometric ratio, and may soon reach a high velocity. If, for instance, the temperature is raised only by 240° the original rate will be multiplied by 2^{24} or 16,777,216, which means that an action which originally took more than *six months* will now take place in *one second*. The explanation of those “spontaneous combustions” which are reported from time to time as mysteriously occurring in tightly packed haystacks or cargoes of coal may be found in these facts. Exothermic combination occurs between the hay, or coal, and the oxygen of the air, but proceeds very, very slowly at ordinary temperatures. If, however, at some particular spot the heat evolved does not escape (owing to absence of air currents or any other cause), the temperature at that spot will

rise; this rise of temperature will accelerate the action; the increased amount of action will be attended by increased evolution of heat, which in turn will cause increased rise of temperature, and so on, in a "vicious cycle," till the action becomes a fire. Conversely, a *reduction* of temperature *retards* chemical action, and at the very low temperatures more recently reached, in the neighbourhood of -200° C., this action is almost arrested.

NATURE OF HEAT—ENERGY—CONSERVATION OF ENERGY

In the preceding paragraph, as well as in that referring to *latent heat* (p. 4), the relation of heat to chemistry has been sufficiently indicated for the present purpose, although we have by no means exhausted the subject. Indeed, this relation is now regarded as so intimate and extensive that whole text-books are devoted to *thermal chemistry* in which this aspect of the science is specially studied. We shall proceed now to consider the *nature* of heat. Heat is now regarded not as something *unique*, but as one of the many forms of **energy**.

We are unable to create energy or to destroy it, but we are often able to convert one form of energy into another; thus we frequently convert chemical energy into electrical, and vice versa. When, for instance, we work a Grove's or a Bunsen's cell, the element zinc dissolves in the sulphuric acid with formation of a new compound, the sulphate of zinc. While the zinc and sulphuric acid existed apart, the world possessed a certain amount of *potential* energy. After combination this potential energy is lost to the world.

In return for the sacrifice of this, which we may call *chemical* energy, since its disappearance is connected with the formation of a chemical compound,

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we obtain a supply of *electrical* energy which may be used to send a current of electricity through a wire, thus heating the wire and transforming some of the original energy into the *heat*-form. Or the current may be made to flow round a soft iron bar and thus magnetise it, and the magnet may be used to draw a hammer on to a bell, as in the ordinary electric bell, thus spending itself in *kinetic* (*κίνησις*, to move) and *sonorous* energy.

There seems, indeed, hardly any limit to the number of transformations that energy may undergo. The evolution, or absorption, of heat is therefore the evolution or absorption of energy, and latent heat must really mean latent energy. What becomes of this energy? It is expended in converting, for instance, a liquid into a gas; in doing work upon the molecules of the liquid, dissociating them, probably, into lighter and less complex molecules, and giving them also greater freedom of motion. When the gas is condensed to a liquid, this latent energy becomes again available as a source of work. The statement that energy can neither be created nor destroyed, or that the supply of energy in the universe is constant, is known as the law of **conservation of energy**. This law is of the greatest importance, and of the widest possible application, in the study of matter. Matter appears to be merely, as it were, the plaything of energy—the field in which energy lives and moves and has its being—the body of which energy is the informing spirit. Energy itself is not matter. We have seen that it may assume many forms, the heat-form, the electrical form, the chemical form, etc.; but, that we may avail ourselves of it, one condition must apparently exist. This condition will be more apparent if we consider one or two examples.

A water-fall is a source of energy, for it may be

made to turn a windmill, drive a dynamo, generate an electric current, and thus perform work of varied kind. But if all the water in the world were at the same level, and we had no means of creating a difference of level, this source of energy would be unavailable to us. The availability therefore of this energy depends on the fact that water is at different levels in different places, and that it tends to flow from a higher to a lower level.

Again, electricity tends to pass from points at a higher electrical level or "potential" to points at a lower level, and, by virtue of this tendency, we can obtain an available form of electrical energy so long as points can be found between which a difference of electrical potential exists. But if all matter were electrified to the same potential, and we could not create difference of potential in any way, this source of energy would not be available to us; we should probably not discover its existence.

One more example. The availability of heat as a source of energy depends on a difference of heat-level or "temperature," as it is always called, and on the fact that heat tends to pass from a body at higher temperature to a body at lower. If two bodies (regarded for the moment as an isolated material system) are at the same temperature, neither gains nor loses by exchange of heat; but if there is an initial difference of temperature, then an unequal exchange takes place, by which the hotter loses and the colder gains, till thermal equilibrium is attained. When, therefore, this difference of level exists we can transfer a nett amount of heat—and therefore of energy—to the colder body. But if all bodies were at the same temperature and doomed to remain so, this source of energy would also be closed to us.

In these three instances we cannot fail to observe a striking analogy. The condition which appears

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to be essential in order that the energy may be available to us is *difference of level, difference of potential, difference of temperature.*

POSITIVE AND NEGATIVE ELEMENTS

The student of chemistry will naturally inquire whether this analogy extends into his particular field also. Do we find as a condition prior to the manifestations of chemical energy anything corresponding to this difference of level?

If the law of conservation of energy is as comprehensive as we believe, we must expect an affirmative answer to this question. Our expectation is confirmed when we examine the circumstances under which the most familiar manifestation of chemical energy—chemical combination—takes place. We are then compelled to observe the following facts: One element does not combine with equal readiness with all the others. It combines most readily with those that contrast most strongly with itself, and therefore, we may say, when the greatest difference of level exists. Thus potassium shows no desire to combine with sodium, an element closely resembling itself; but, on the other hand, combines eagerly with oxygen or with chlorine, elements so unlike potassium that they and others like them have been called **negative** elements, while potassium and sodium and others of the same character have been called **positive** elements. As we proceed with our study of chemistry we shall see how well this distinction is deserved, for the contrast is maintained in their compounds, and gives rise to very important results.

CHEMICAL ATTRACTION

Just as difference in electrical potential is the source of electromotive force, so also it now appears that this difference in character, so favourable to the dis-

play of chemical energy, is the source of that peculiar force which has been named *chemical attraction*. This force, we must remember, acts between the smallest particles of matter, and only at inappreciable distances. This condition is most easily secured if one, at least, of the substances engaged is in the liquid or gaseous state, sufficiently close approximation of the particles of two solids being difficult to effect.

An example of the last-mentioned fact is obtained by powdering and rubbing together in a mortar tartaric acid and carbonate of soda; no change whatever occurs; but if water be now added to the mixture in the mortar, the two substances will dissolve, and in the dissolved state will come sufficiently close to one another to react, chemical action being manifested by the effervescence that takes place, due to the tartaric acid acting on the carbonate of soda, forming tartrate of soda, and liberating carbonic acid gas.

CHAPTER II

CHANGES OF MATTER—SYMBOLIC CHEMISTRY

Matter indestruetible—Analysis and Synthesis—Metals and Non-metals—Symbols—Atomic Weight—Atomic Theory—Formulae—Equations—Valency—Compound Radicles.

Indestructibility of matter.—The student has already learned that energy is never *destroyed*, but that its apparent destruction is really a *transformation*. Matter is not energy, but it is a significant fact that this remarkable feature is common to both. Matter is never really destroyed. When a candle burns away, the *candle* is destroyed, but the *matter* of which the candle was composed *still exists in other forms*; the carbon has combined with the oxygen of the air to form carbon dioxide, and the hydrogen to form water.

Analysis and synthesis.—The study of these transformations of matter is the immediate object of chemistry. They are effected by one of two processes, either by the decomposition of complex substances into simpler ones, which is called **analysis** (ἀνάλυσις, loosening), or by the joining together of simpler substances to form one more complex, which is called **synthesis** (σύνθεσις, putting together). Analysis begins with compounds and leads ultimately to elements. Synthesis begins, if possible, with elements and builds up compounds.

Metals and non-metals.—Chemistry has en-

abled us to distinguish some eighty different elements. Our classification of them as **positive** and **negative** coincides very closely with the more familiar division into **metals** (positive) and **non-metals** (negative). As usual, however, with Nature's classifications, the border line between the two classes is not rigid and precise. The two types of elements gradually merge into and blend with one another, and only the far-separated members of the two classes possess any well-marked distinguishing characters. A few of the best-marked characters, and those that may be most readily recognised, are the following :—

Metals possess, or can be made to possess by polishing or by powerful compression, a peculiar surface, known as *metallic lustre*—a property that is well known to everyone. It is true that metals in a fine state of division, such as the reduced iron of the British Pharmacopœia, do not possess this lustre, but if by powerful pressure or hammering they are compressed into a mass, and this mass be polished, the metallic lustre is then developed. There are two of the common metals which are coloured, viz. **copper**, which is of a reddish colour, and **gold**, which is of a yellow colour. Non-metals are destitute of the peculiar surface known as metallic lustre ; it is impossible to develop a mirror-like surface on a stick of phosphorus or on a piece of sulphur ; the only non-metallic elements that possess anything like a metallic lustre are *iodine* and *carbon* (in the form of graphite). Metals are also good conductors of both heat and electricity, whereas non-metals are extremely bad conductors of these two forces. The oxides of the metals as a rule form bases, those of the non-metals acids. This chemical distinction provides the most reliable test of the chemical character of an element, and it is on this and other *chemical* grounds that we class arsenic as a non-metallic or

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negative element, although in *physical* features it rather resembles the metals.

State of aggregation of the elements.—At ordinary temperatures ten elements are gaseous—viz. *hydrogen, oxygen, nitrogen, chlorine, fluorine, helium, neon, krypton, xenon, and argon*. Two, *mercury and bromine*, are liquid at ordinary temperatures; the remaining elements are solids. The physical condition of any element can, however, be altered—e.g. sulphur, page 5; the elementary gases can be liquefied by subjecting them to powerful pressure and extreme cold; the feat of condensing oxygen and nitrogen to liquids was accomplished in the latter part of 1877 by Cailletet and by Pictet, these gases having up to that time resisted all attempts to liquefy them. Hydrogen has been liquefied by Olszewski and by Dewar. The two liquid elements, mercury and bromine, can in their turn have their physical condition altered; thus, on being boiled they become converted into vapours or gases, and by exposure to sufficiently low degrees of cold they freeze, or assume the solid state (for instance, mercury frequently freezes in Arctic regions). Most of the solid elements undergo an alteration of state on the application of heat. Thus metals, when heated, melt or liquefy, and further, on the application of an intense heat, volatilise or form vapours.

SYMBOLS.

Many elements are familiar to us, as zinc, copper, nickel, iron, mercury, aluminium, carbon; and as we often have to refer to them it is convenient to do so by abbreviated symbols. The symbol chosen is sometimes the first letter of the name; thus carbon is denoted by C. To avoid ambiguity we cannot now use C for copper, which is therefore denoted by Cu, the first two letters of the Latin name *cuprum*.

Similarly S is the symbol for sulphur, but for silver we use Ag, from “argentum.” I represents iodine, but iron is represented by Fe, from “ferrum.” Other illustrations will be found in the following table:—

<i>English Names.</i>			<i>Latin Names.</i>			<i>Symbols.</i>
Antimony	Stibium	Sb
Copper	Cuprum	Cu
Gold	Aurum	Au
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Mereury	Hydrargyrum	..		Hg
Potassium	Kalium			
			(Arabie name) ..			K
Silver	Argentum	Ag
Sodium	Natrium			
			(Arabie name) ..			Na
Tin	Stannum	Sn

ATOMIC WEIGHT

Some advantage would be gained by the use of these symbols even if they meant no more than has been suggested already. They, however, mean much more, and the abbreviation is much greater than appears at present, because *each symbol represents a definite weight of the element it stands for*; thus C does not represent *any* weight of carbon we please, but always 12 parts by weight. We can therefore represent 24 parts by weight of carbon by C_2 and 36 parts by C_3 , and so on. But how shall we represent a weight which is *not* a simple multiple of 12? *We never require to represent such a weight.* For chemical purposes carbon seems obliged to exist in weights which are either 12 or simple multiples of 12. This is a very remarkable fact, and becomes

even more remarkable when we find that each element appears to be associated with some special weight, just as carbon is with the weight 12. In the case of sulphur this weight is 32, and other examples will be found in the table of international atomic weights on page 87.

The student should learn and remember the two following definitions of this constant:—

1. **The atomic weight of an element is the smallest part by weight of that element which is present in the gaseous molecule of any compound.**

2. **The atomic weight of an element is that weight of the solid element which has the same thermal capacity as 108 parts by weight of solid silver.**

ATOMIC THEORY

It may be well, at this point, to caution the student against offering as a *definition* of *atomic weight* the equivalent expression *weight of an atom*. This is only the old phrase in a slightly varied form, and leaves untouched the real difficulty which is involved in the term **atom**. This word is derived from the Greek, and means literally something that cannot be cut or divided. It was adopted in accordance with a belief that matter is incapable of infinite subdivision without loss of properties; that carbon, for instance, could not be subdivided beyond a certain limit without ceasing to be carbon at all; that, in fact, **to possess all the properties of carbon a certain mass of carbon is required.**

The theory here briefly stated is the famous **atomic theory**, which has dominated chemistry for the last hundred years. It is especially associated with the name of John Dalton.

In accordance with this theory an atom is the

smallest mass of an element which possesses all the properties with which that element is identified. It must therefore possess weight and extension, and be able to exhibit also the chemical capabilities of its kind. Recent theories of the constitution of matter have tended to deprive the atom of this traditional indivisibility, and to separate it into varying numbers of smaller units—*corpuscles*, *electrons*, etc. None of these theories, however, has yet attained a sufficiently stable form to entitle it to a place in a text-book like the present, which must, if possible, contain nothing which the student will require to *unlearn*. Our definitions of the atom only assert that subdivision would entail the loss of one or more of the sum total of properties possessed by the element in mass. That assertion seems likely to remain true whatever form these new theories may ultimately take.

FORMULÆ

We shall discuss in a later chapter some of the methods by which the present *atomic weights* have been determined. It must, however, be stated now that these weights are not absolute; they are *relative*, and only tell us how much the atom of one element is heavier or lighter than the atom of another. The lightest element known to us is *hydrogen*, and the weight of an atom of hydrogen is generally taken as the unit in which the weights of other atoms are expressed. Thus the statement "the atomic weight of carbon is 12" really means, "the atom of carbon weighs 12 atoms of hydrogen," or "weighs 12 times as much as one atom of hydrogen weighs." What one atom of hydrogen actually *does* weigh we do not know. We know that it does not weigh an ounce, or a gramme, or any weight that we can appreciate; but, whatever it does weigh, the atom of carbon

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weighs 12 times that weight, the atom of sulphur weighs 32 times that weight, and so on.

Having now at our disposal a set of symbols to represent the *elements*, we can clearly combine them in various ways to represent the various *compounds* that may be formed by the union of any two or more of these elements. Any such combination of symbols is called a **formula**. Thus the formula assigned to water is H_2O because this combination of symbols expresses in our chemical shorthand the proved composition of water (*see* page 115).

EQUATIONS

The changes that occur when two or more substances act chemically upon one another can now be represented by placing on the left the formulæ of the substances as they exist *before* the change, connected by the sign $+$, signifying, as in algebra, addition of one to the other; on the right are formulated the substances as they exist *after* the change, connected together, as before, by the sign $+$. The two expressions are then connected by the sign of equality $=$. The whole symbolic statement is known as a **chemical equation**. A thorough knowledge of the representation of chemical reactions by means of equations is absolutely necessary, and careful attention should be given to this subject. It is more fully discussed in Chapter V.

VALENCY

Atoms differ not only in weight but in **valency**.* By virtue of this remarkable property they differ in exchange value, as coins do. Just as *one* three-penny coin may be exchanged for *three* penny coins, so *one* aluminium atom may be exchanged for *three*

* *Atomicity* and *quantivalence* are other names used to denote this same property.

hydrogen atoms. As the hydrogen atom seems to possess unit valency and to correspond to the penny coin in our chemical currency, it is called a **monad** or monovalent atom. The aluminium atom is therefore a **triad** or trivalent one. It seems possible for valency to have any integral value from 1 to 8.

Variation in valency.—It is, of course, possible with a sixpenny coin to employ only a part of its purchasing power and to hold the remainder in reserve. In this respect also the valency of an atom corresponds to the purchasing power of a coin. A pentavalent atom, such as the nitrogen atom, may, for instance, use only a part of its full valency and hold the remainder in reserve in some way. We must, however, regard the *maximum* valency of an atom as its *true* valency, and account for its exercise of lower valencies in this way; when an atom is exerting its maximum valency, the compound it forms is said to be **saturated**. Such compounds appear to be more stable than **unsaturated** ones. The valency of an atom may be measured, not only by the number of hydrogen atoms for which it can be exchanged, but also by the number of hydrogen atoms with which it can combine. Instances of a higher valency than eight are unknown, and the polyvalent elements seem only to exert their maximum valency on rare occasions. Thus phosphorus forms PH_3 in preference, apparently, to PH_5 , and sulphur SH_2 in preference to SH_6 . SO_3 is, however, a well known compound, and since oxygen never seems to exert a lower valency than 2, we argue that sulphur has here a valency of 6. Similarly, from P_2O_5 we argue that phosphorus is a pentad. Facts like these teach us that there is something more than a mere *numerical* difference between valency towards one element and valency towards another. They suggest that valency is really a dual or re-

ciprocal relation, and that the nature of each partner influences the bond of partnership.

RELATION OF VALENCY TO CHARACTER

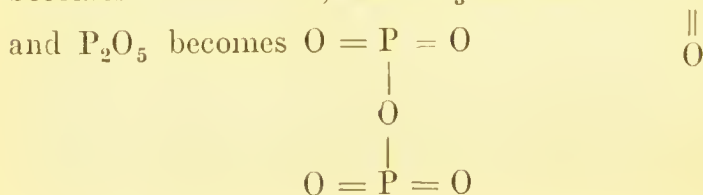
There seems to be some subtle connection between valency and character; high valency is usually associated with a negative element, and low valency with a positive one. Even when the same element has two valencies, this distinction is observed. Chromium when hexad resembles sulphur (a negative element), but when triad it resembles aluminium (positive).

GRAPHIC REPRESENTATION OF VALENCY







The valency of an atom is sometimes represented, by small dashes or by Roman numerals placed over its symbol, thus :

Monad or monovalent	H ⁱ
Dyad or divalent	Hg ⁱⁱ
Triad or trivalent	Fe ⁱⁱⁱ
Tetrad or tetravalent	C ^v
Pentad or pentavalent	P ^v
Hexad or hexavalent..	S ^{vi}
Heptad or heptavalent	Mn ^{vii}
Oetad or octovalent	Os ^{viii}

In order to indicate to the eye the actual arrangement of the atoms in a compound, straight lines are drawn between the symbols, indicating the connections which are believed to exist. We thus obtain a *graphical formula* of the compound. Thus H₂O becomes H — O — H, and SO₃ becomes O = S = O



These lines, equal in number to the valency of the atom, are often attached to the symbols of the elements, thus :—

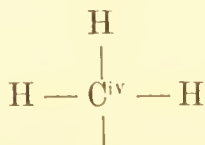
Monad	H—
Dyad	—Hg—
Triad	
Tetrad	
Pentad	
Hexad	
Heptad	
Octad	

It is scarcely necessary to caution the student against supposing that elements actually have arms projecting from them. These lines do not, of course, represent anything material. But we have already mentioned the force of chemical attraction as acting between atoms. Now a *force* must have *direction*, and this direction can be represented by a line. There is nothing grotesque, or even unreasonable, in regarding these lines as representing, numerically, the directions in which this force may act. It certainly suggests that a monad can only exert force in *one* direction at a time, a dyad in two directions, a triad in three, and so on ; and this may be perfectly true.

We can, for instance, conceive of the existence of one or more separate centres of attraction. If we suppose the number of these centres to be capable of increase or diminution, by subdivision or coalescence respectively, we have a plausible explanation of change of valency.

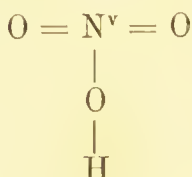
COMPOUND RADICLES

The term **compound radicle** is used to denote an unsaturated group of atoms which, by virtue of its unemployable valency, is able to play the part of a single atom. These compound radicles therefore function as elements; they also show the same difference of character. We have *positive* ones like the group—



and these are of great importance in organic chemistry. We have also *negative* ones, like $\text{O} = \text{N}^{\text{v}} = \text{O}$, the

radicle of nitric acid, whose graphical formula is



These negative radicles are frequently termed *acid radicles*, because in combination with hydrogen they give rise to *acids*. The two compound radicles mentioned are both monad, but others of higher valency will be referred to later.

CHAPTER III

MOLECULES

The Molecule—Avogadro's Law—Determination of Molecular Weights (*a*) of Gaseous (*b*) of Dissolved Substances—Determination of Atomic Weights (*a*) of Gaseous (*b*) of Solid Elements—Abnormal Molecules—Abnormal Vapour Densities—Determination of Equivalents.

OUR first definition of atomic weight (page 20) assumes that there is a minimum limit to the weight of an element which enters into the molecule of a compound; that, for instance, less than 12 parts by weight of carbon does not enter into the molecule of any compound of carbon. We do not name these "parts by weight"; we only say that the hydrogen atom weighs one of them. Now if this is true of *elements*, it must also be true of the *compounds* they form. There must be a minimum limit of weight in this case also. If *less* than 40 parts by weight of calcium or *less* than 16 of oxygen cannot combine, then *less* than 56 parts of calcium oxide cannot be formed. Corresponding then to the minimum mass of *element* which we called "atom," there must be a minimum mass of *compound*, and this we call **molecule**. Dalton saw the correspondence so clearly that he called it "compound atom," but it is more convenient to restrict the term "atom" to elements. We do not, however, restrict the term "molecule" to compounds. There are some grounds for believing that although a single atom of an element can exert chemical activity, it cannot, in general, enjoy an

independent existence. Thus, when a piece of sodium is dropped into water, energetic action takes place, and hydrogen gas is evolved. The water, neutral before, is now found to be strongly alkaline, and to have become in fact a new substance. H_2O has become NaOH . An atom of sodium has displaced an atom of hydrogen.



Although the single atom of hydrogen may thus be driven out, it does not remain single for any appreciable time, but at once associates itself with a fellow-atom of hydrogen, and the two seem then to pursue an independent existence so long as no more attractive partner comes within range. This little group of two we call a molecule of hydrogen. **A molecule is the smallest mass of any substance, elementary or compound, capable of independent existence.**

DIATOMIC MOLECULES

In the case of a *compound*, it is clear that the molecule must contain at least *two* atoms. Thus hydrochloric acid, which is a compound of *two* elements, chlorine and hydrogen, must contain at least *two* atoms, one of each kind, since, by hypothesis, less than one atom of any element cannot enter into combination at all (page 20). The molecule of hydrochloric acid must therefore contain *at least* two atoms. But how can we say this of the hydrogen molecule, which contains only *one* element, and possibly therefore only *one* atom? We shall find the answer to this question in a single experiment interpreted by the light of a great generalisation which we owe to an Italian chemist, Avogadro. It was first published in 1811, when the author was 35 years of age.

AVOGADRO'S LAW

Equal volumes of all gases, measured at the same temperature and under the same pressure, contain the same number of molecules.

Now if we take such *equal volumes* as are here described, of the two gases hydrogen and chlorine, allow them to mingle and expose them to light, they readily combine to form a new gas—hydrochloric acid. This new gas fills exactly the whole space before filled by the *two* elementary gases, or, in fact, has *twice* the volume that either elementary gas had.

Now let us suppose that the volume of hydrogen taken contained a certain number n of hydrogen molecules. Then by Avogadro's law the *equal* volume of chlorine taken contained the *same number* n of chlorine molecules, and the *double* volume of HCl obtained must, by this law also, contain a *double* number of HCl molecules.

Therefore n molecules of hydrogen + n molecules of chlorine yield $2n$ molecules of HCl. But each molecule of HCl contains *at least* 1 atom of hydrogen and 1 atom of chlorine. Therefore $2n$ molecules of HCl contain *at least* $2n$ atoms of hydrogen, and $2n$ atoms of chlorine. We have, then, $2n$ atoms of hydrogen. Where could they come from? Not from the molecules of chlorine, for, by hypothesis, chlorine is an element, and can yield no other element. These $2n$ atoms of hydrogen must therefore have come from the n molecules of hydrogen. Therefore each molecule of hydrogen must contain *at least two* atoms of hydrogen. It is clear that the same reasoning shows that the chlorine molecule contains at least two atoms of chlorine. For these reasons we represent the molecule of hydrogen by H_2 , and of chlorine by Cl_2 . By similarly interpreting the

results of other experiments, we obtain information about other gases. Thus 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam H_2O , or $2n$ molecules of hydrogen + n molecules of oxygen yield $2n$ molecules of H_2O , which must contain *at least* $2n$ atoms of oxygen. These $2n$ atoms of oxygen can only have come from the n molecules of oxygen. Therefore one molecule of oxygen must contain at least two atoms, and be represented by O_2 . The molecules of many elements in the gaseous state contain two atoms, and are called diatomic. Some exceptions are discussed later (page 44).

MOLECULAR WEIGHT

We must now refer to another important application of Avogadro's Law. Dry carbon dioxide gas has been found to weigh 22 times as much as an equal volume of dry hydrogen gas *measured under the same circumstances of temperature and pressure*. But, by Avogadro's law, this means that n molecules of CO_2 weigh 22 times as much as n molecules of hydrogen, and therefore that 1 molecule of CO_2 weighs 22 times as much as 1 molecule of hydrogen.

If, then, we know what 1 molecule of hydrogen weighs, we shall know what 1 molecule of CO_2 weighs. Now we do not know what 1 molecule of hydrogen really *does* weigh, but we have seen that it contains at least 2 atoms of hydrogen, and we have already used the weight of 1 atom of H as our unit weight, in terms of which the other atomic weights are expressed. We now see that this unit will still be useful, for the molecule of hydrogen evidently weighs at least two of these units, and we shall therefore call the molecular weight of hydrogen 2. But we have seen that the molecule of CO_2 weighs 22 times the molecule of hydrogen ;

therefore, in terms of our unit, the molecular weight of CO_2 is 44.

We arrive now at this important conclusion :—

To find the molecular weight of any substance in the gaseous state.—**Find the density (d) of the gas compared with hydrogen; then, by Avogadro's Law, the molecular weight of the substance is $d \times 2$.**

The gramme-molecule.—It has been found that 2 **gram.** of hydrogen fill, at 0° and 760 mm., a volume equal to 22.4 litres, which is rather less than 5 gallons. The same volume of a gas which is d times as heavy as hydrogen must therefore weigh $d \times 2$ **gram.**; this is the same *number* as we have just found to represent the molecular weight of the gas, but the *unit* to which the number refers is very different in the two cases. The molecular weight is $d \times 2$ times the weight of *one atom of hydrogen*, but the weight of these 22.4 *litres* is $d \times 2$ times the weight of 1 *gram*. If then M be the molecular weight of any gas, we may say that M gram. of this gas will fill 22.4 litres at N. T. P.* As the ordinary formula of a substance represents a molecule, this important fact is sometimes stated as follows : **The formula weight in grammes of a substance will fill, in the gaseous state, 22.4 litres at N.T.P.** The student will find the statement of great assistance in many chemical calculations. The formula weight in grammes or the molecular weight in grammes is sometimes referred to as one *gramme-molecule*, and has also been called one *mole*.

* N. T. P. is a useful abbreviation for "normal temperature and pressure," and means at 0° C. and under a pressure of 760 mm. of mercury.

DETERMINATION OF THE MOLECULAR WEIGHTS OF GASEOUS SUBSTANCES

From what has been said, it is clear that the most direct road to the determination of the molecular weight of a substance is to find the weight in grammes of 22.4 litres of the gaseous substance at N. T. P. This problem is not quite so simple in practice as might be supposed, but it is materially simplified by the fact that this weight can be deduced from the weight of *any* volume of the gaseous substance collected at any temperature and pressure. This is due to the operation of two important laws, which must now be considered :—

1. Boyle's Law.—The volume of a gas varies inversely as the pressure when the temperature remains constant.

This means that if a certain mass of gas occupies a volume V under a pressure P , then under a *new* pressure P' the *same mass* of gas will fill a new volume V' such that

$$\frac{V}{V'} = \frac{P'}{P}$$

and therefore $VP = V'P'$, the temperature being unchanged.

2. Law of Charles and Gay-Lussac.—The volume of a gas varies directly as the absolute temperature when the pressure remains constant.

The *absolute* temperature is the ordinary centigrade temperature *increased by* 273, and is commonly represented by T . This law therefore means that if a certain mass of gas occupies a volume V at the absolute temperature T , then at a new abso-

lute temperature T' the *same mass* of gas will fill a new volume V' such that

$$\frac{V}{T} = \frac{V'}{T'}$$

the pressure being unchanged.

Combining these two results, it follows that, when both pressure and temperature may vary, we shall have always

$$\frac{VP}{T} = \frac{V'P'}{T'}$$

The following example will illustrate the application of this important equation: 25.3 c.c. of a gas measured at 21.5° C. and 699.5 mm. weighed .073 gm. What would be the weight of 22.4 litres at N. T. P. ?

In this case,

$$\begin{array}{lll} V' = 25.3 \text{ c.c.} & P' = 699.5 & T' = 294.5 \\ V = ? & P = 760 & T = 273 \end{array}$$

$$\text{and therefore } \frac{V \times 760}{273} = \frac{25.3 \times 699.5}{294.5}$$

whence we find $V = 21.5$ c.c.

We now know that

21.5 c.c. at N. T. P. weigh .073 gm.

and \therefore 1 c.c. „ weighs $\frac{.073}{21.5}$ „

\therefore 1 litre (=1,000 c.c.) „ „ $\frac{73}{21.5}$ „

\therefore 22.4 litres „ weigh $\frac{73 \times 22.4}{21.5}$ gm.

that is, 22.4 litres at N. T. P. weigh 76.0 gm.

The density of the gas, referred to hydrogen, is therefore 38, and the molecular weight is 76.

In the case of substances which, like CO_2 , are generally found in the gaseous state,

the densities have been very carefully determined by Regnault and others. The methods employed are usually described in detail in text-books of physics. It should, however, be mentioned here that the density, as found by these experiments, is *referred to air*, and must be multiplied by 14.435 to give d , the density *referred to hydrogen*, because air is 14.435 times as heavy as hydrogen.

Ex.—Density of CO_2 (air = 1) is 1.529

∴ „ „ (H = 1) is 1.529×14.435

∴ Molecular weight of CO_2 ($d \times 2$) = 1.529×28.87

If therefore we use the values of the densities (air = 1), we must multiply them by 28.87 to obtain the molecular weights. This is commonly done.

In the case of substances which are not gaseous at ordinary temperatures but can, without decomposition, be brought into that state, the density may be determined by an ingenious method which is due to Victor Meyer. A tube about two feet long is expanded at its lower end into a bulb A (Fig. 1); it is closed at its upper end with an india-rubber cork, and has a short delivery tube B inserted a short distance below the cork; the delivery tube ends in a trough D filled with water. The tube A is placed in an outer tube whose bulb is about half filled with a suitable liquid; water, aniline, and molten tin have been used. This liquid is heated to a temperature well above that at which the substance chosen for experiment would be vaporized. Air at first escapes through B; but is not collected. As soon as bubbles cease to escape, the cork is removed and a weighed quantity, about 0.1 grm., of the substance contained in a small bulb (*see* Fig. 41) or little stoppered tube is dropped into A, and the cork immediately replaced. The substance is at once converted into vapour,

which displaces some of the air, and this displaced air is collected in the graduated tube c, which has been placed over the end of the delivery tube.

The temperature and pressure of the air in the neighbourhood of c at the time must be carefully noted, as the volume of air collected must be reduced to N. T. P. The level of the water in c is, at the close of the experiment, above that in D, and a correction is required on this account. It is most easily made by closing the open end of c with a well-fitting, greased plate, and then transferring the tube to a deeper vessel in which it can be depressed till the water is at the same level, both inside and outside. The pressures of the air inside and outside must therefore be the same, and are given by the barometer in the room. The inside air is, however, saturated with aqueous vapour, and part of the pressure it exerts is due to the tension of this vapour; this is found from tables, and must be *deducted* from the barometer reading.

Ex.—.073 gm. of ether displaced 25.3 c.c. of air, measured at 21.5° C., and pressure .718.6 mm., the tension of aqueous vapour at 21.5° C. is 19.1 mm.; the pressure due

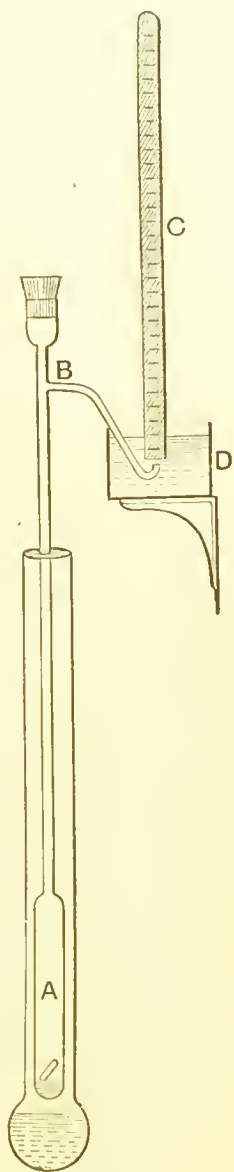


Fig. 1.—Victor Meyer's vapour-density apparatus.

to the air only is therefore $718.6 - 19.1 = 699.5$ mm. The conditions are the same as in the problem solved on page 33, and lead as before to the molecular weight 76. (The value, calculated from the formula of ether, is 74.)

DETERMINATION OF MOLECULAR WEIGHTS OF DISSOLVED SUBSTANCES

There are, however, solid substances which either cannot be made gaseous at convenient temperatures or without undergoing decomposition. Victor Meyer's method is not applicable to them, and we have recourse to others. When a solid is dissolved in water, or some other solvent, the freezing-point and boiling-point of the solution are no longer quite the same as those of the pure solvent. Sea-water, for instance, does not freeze so easily as fresh water, because it holds so much salt in solution. The freezing-point is lowered, and the boiling-point is raised. These facts have been familiar for ages, but their quantitative nature and its significance have only quite recently been appreciated. Raoult and others have established the remarkable fact that if a molecular weight in grammes of a substance is dissolved in 100 grm. of a suitable solvent, the depression of the freezing-point produced is always—within certain limits—the same, *whatever the nature of the substance*. This depression is therefore a constant for any one solvent; for water it is 19, for glacial acetic acid 39. It is denoted by the letter K. It has also been proved that, if the solution is dilute, *the depression produced is proportional to the weight of the substance dissolved*; thus, if 1 grm. of a substance dissolved in 100 grm. of a solvent produces a depression of $.06^{\circ}$, 2 grm. will produce a depression twice as great, $.12$, etc.

	Grm. of substance.	Grm. of solvent.	Depression of freezing-point.
So if	p	dissolved in 100	produce D
we argue that	1	„ 100	will produce $\frac{D}{p}$
and	M	„ 100	„ $\frac{M \times D}{p}$

but if M is the molecular weight of the substance, we know that it should produce the depression K , therefore we have

$$\frac{M \times D}{p} = K$$

or

$$M = \frac{K \times p}{D}$$

As an example, 13.68 gm. of dextrose were dissolved in 100 gm. of water, and produced a depression of 1.45° .

$$\text{Molecular weight} = \frac{19 \times 13.68}{1.45} = 179.9.$$

The molecular weight calculated for $C_6H_{12}O_6 = 180$.

The experiment is usually conducted in an apparatus designed by Beckmann. It consists of a stout glass vessel A (Fig. 2), which contains cold water, ice, or ice and salt, according as glacial acetic acid, benzene, or water is used as the solvent. In this is fixed a large test-tube B , furnished with a wide side-tube C , which is closed by a cork. The upper end of the tube B is also closed by a cork, through which pass a delicate thermometer D , divided into $\frac{1}{100}$ ths of a degree, and a platinum wire E , bent at its lower end to form a stirrer. The lower end of B is surrounded by an empty tube F , which serves as an air-jacket, and ensures a *gradual* change of

temperature. A known weight of the solvent (usually water or glacial acetic acid) is introduced into the tube B, which is then immersed in the cooling vessel A: the solvent is vigorously stirred, allowed to freeze, and the freezing-point noted. A weighed quantity of the substance is then introduced by the side-tube c, and the experiment repeated, the freezing-point being again noted. The difference in temperature between the two observations gives the lowering of the freezing-point produced by a given weight of the substance.

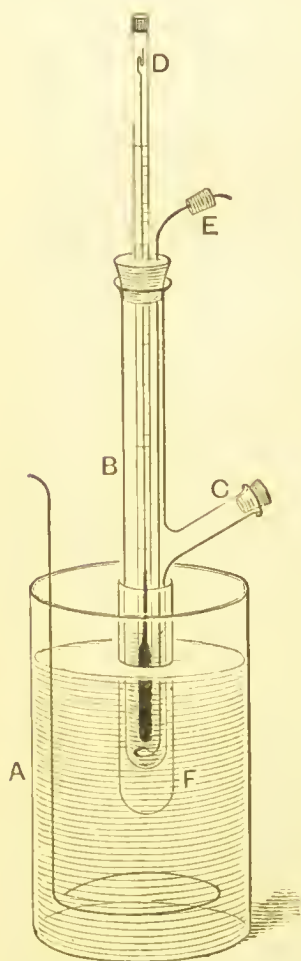


Fig 2.—Beckmann's apparatus for determining the depression of the freezing-point.

A method based upon **osmotic pressure** has also been applied to determine the molecular weights of substances in solution. When two liquids are separated by a porous partition, either may pass through the boundary and diffuse into the other. This process is called osmosis (from $\omega\sigma\mu\acute{o}\varsigma$ = a thrusting). As all liquids do not necessarily osmose to the same extent, the process may result in an unequal distribution of liquid on the two sides of the partition.

Imagine that a vessel v (Fig. 3), with a porous wall of this description, contains a liquid A, and is surrounded by another liquid B contained in the

beaker G . The open end of v is closed by a plug which is pierced by a tube T , open at both ends. If T be clamped as shown, v may be conveniently adjusted in position.

If B osmoses to a much greater extent than A , liquid will accumulate in v and will be forced up the tube T till it reaches a height h , such that the downward pressure of this column of liquid is just equal, and opposite, to the force which is urging B into v ; h will therefore measure this *osmotic pressure*. Now dilute solutions, in which the molecules of the dissolved substance are, so to speak, somewhat thinly scattered throughout the solvent, approximate in character to gases and obey similar laws.

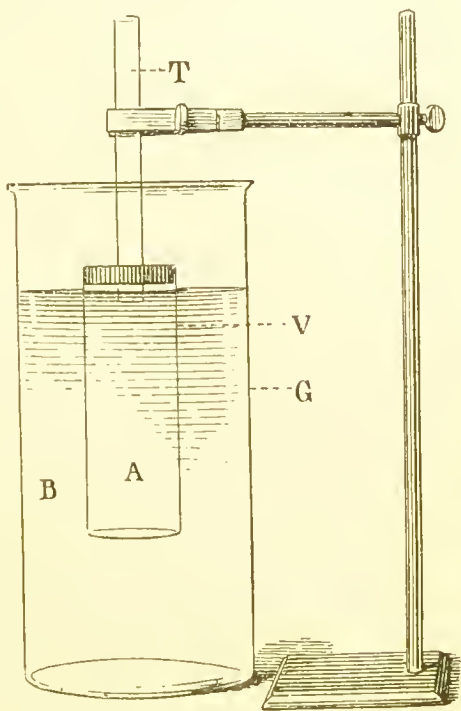


Fig. 3.—Diagrammatic illustration of osmosis and osmotic pressure.

The straight pressure-tube T is reduced in linear scale.

In the case of solutions, however, *osmotic pressure* takes the place of the gas pressure. By extending Avogadro's Law in this sense Van't Hoff enunciated his *law of osmotic pressure*: *Equal volumes of different solutions, at the same temperature and osmotic pressure, contain equal numbers of molecules, which numbers are the same as would be contained in equal*

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volumes of gases at the same temperature and pressure.

We may therefore expect (page 31) that the molecular weight of the solid dissolved in 22.4 litres of the solvent will at 0° C. exert an osmotic pressure of 76 cm. or 1 atmosphere. Measurement of osmotic pressure will therefore enable us to determine molecular weight.

Ex.—Pfeiffer* found that a 1 percent. aqueous solution of cane sugar at 6.8° exerted an osmotic pressure of .664 atmosphere—that is :

	Grm. of Cane Sugar	Vol.	Temp.	Osmotic Pressure in Atmospheres
	1	fill 100 c.c.	at 6.8°	and .664
∴	1†	$\frac{273 \times 66.4}{279.8}$ c.c.	„ 0°	„ 1
∴	$\frac{279.8}{273 \times 66.4}$	„ 1 c.c.		
∴	$\frac{279.8 \times 1000 \times 22.4}{273 \times 66.4}$	„ 22.4 litres	„	
or	345	„ 22.4 litres	„ N.T.P.	
∴ Molecular weight of cane sugar is 345 (the exact value is 342).				

DETERMINATION OF ATOMIC WEIGHTS

1. Of elements known in the gaseous state.—If we know M, the molecular weight of an element, and N, the number of atoms in the molecule, we can at once obtain A, the atomic weight of the element, for evidently

$$A = \frac{M}{N}$$

We have already stated (page 30) that N is generally 2. In this case, $M = A \times 2$; but we have already seen (page 31) that $M = d \times 2$, therefore for elements whose gaseous molecules are diatomic we find $A = d$,

*He used an artificial membrane of precipitated ferrocyanide of copper, and a bent mercury gauge instead of the straight tube T.

† See page 33.

or, the atomic weight is equal to the density of the gaseous element compared to hydrogen. The atomic weights of oxygen, nitrogen, and chlorine, for instance, are easily deduced in this way.

2. **Of elements not known in the gaseous state except in combination.**—The important element carbon is not known in the gaseous state, and its density in that state cannot therefore be compared with that of hydrogen. Carbon does, however, form very many compounds which are gaseous even at ordinary temperatures, and we can therefore find the atomic weight as follows: The definition of atomic weight already stated (1, page 20) really tells us how to deduce the atomic weight of an element when we know the molecular weights of one or more gaseous compounds of the element. We must then ascertain what weight of the element is contained in each of these molecular weights. The various weights of the element, so ascertained, will be found to be integral multiples of the lowest of their number, or to have some other highest common factor. This minimum weight or highest common factor must be chosen as the atomic weight.

Tabulating data for carbon, we have:—

Gaseous Compound examined	d density (H=1)	d × 2 =M mol. wt.	Weight of Carbon found by analysis in M parts by weight of compound
Carbonic oxide	14	28	12
Carbonic anhydride	22	44	12
Methane	8	16	12
Ethylene	14	28	24
Acetylene	13	26	24
Propane	22	44	36

The numbers in the last column are 12 and integral multiples of 12. **We therefore select the smallest number, 12, to represent the atomic weight of carbon.** Many other gaseous compounds of carbon are known, but their examination has hitherto only confirmed this number.

3. Of solid elements, especially those forming few or no gaseous compounds.

Law of Dulong and Petit.—The second definition of atomic weight (2, page 20) indicates a method of obtaining the atomic weight that is especially useful in reference to elements which are *solid at ordinary temperatures*.

In 1819 Dulong and Petit discovered that by multiplying the atomic weights of the solid elements by their respective specific heats they obtained a constant product (about 6.4). Thus :

Silver	108	\times	0.057	=	6.15.
Tin	118	\times	0.0562	=	6.6.
Iron	56	\times	.114	=	6.4.
Platinum	195	\times	.0325	=	6.4.
Bismuth	208	\times	.0318	=	6.4.

The slight variations in the constant value obtained are due to the fact that the specific heat is not exactly the same at all temperatures, but tends rather to increase with rise of temperature up to a certain point at which it reaches a maximum. It is probable that, if this constant maximum value of the specific heat were used, these variations would disappear, and we should find in all cases

$$\text{Atomic weight} \times \text{specific heat} = \text{the same constant (about 6.4).}$$

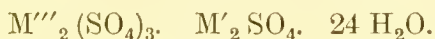
If, therefore, we find the specific heat (S) of the solid element, we shall have

$$\text{Atomic weight} = \frac{6.4}{S}$$

As the product, mass \times specific heat, is the *thermal capacity* of the mass, Dulong and Petit really established the significant fact that **all atoms have the same thermal capacity.**

Isomorphism.—A third method of determining atomic weights is based upon isomorphous relations as investigated by Mitscherlich. When different substances assume the same crystalline form, they are described as isomorphous. The isomorphism may be so perfect that a crystal of one substance will grow in a solution of the other, and crystals of mixed composition be obtained. When this happens **the replacement of one substance by the other is always in molecular proportions,** in accordance with Mitscherlich's **law of isomorphism.** We therefore infer identity of atomic arrangement from identity of crystalline structure, and this may lead to a value of the atomic weight, as indeed it did in the case of gallium.

Ex.—Gallium sulphate formed a double compound with ammonium sulphate, isomorphous with the alums, and therefore having, in all probability, the general formula



In ammonium alum M' is NH_4 and M''' is Al. Therefore in the gallium compound M' is NH_4 and M''' is Ga. Analysis shows that the weight of gallium present in as much of this compound as contains $4(SO_4)$ is 138. But this must be, from analogy, *two* atoms. Therefore, the atomic weight of gallium must be 69. This value was afterwards confirmed by other methods.

ABNORMAL MOLECULES

The relation $A = \frac{M}{N}$, which was arrived at on

page 40, will evidently tell us the value of N now that we can obtain independent values of A and M by the methods described. In this way we shall discover whether the gaseous molecule of an element is **diatomic** and, if not, whether it contains more or less than two atoms.

Ex.—The atomic weight of phosphorus is 31, deduced like that of carbon, on page 41, from similar data. But the molecular weight of phosphorus vapour is 124, for d ($H = 1$) is found to be 62, and $d \times 2 = 124$. Hence $A = 31$ and $M = 124$, and therefore

$$31 = \frac{124}{N}$$

whence we find at once $N = 4$. The gaseous molecule of phosphorus is therefore **tetratomic** and must be represented by the symbol P_4 . Similar evidence has proved that the molecule of arsenic, an element which bears a close chemical resemblance to phosphorus, is also tetratomic.

On the other hand, the molecular weight of mercury deduced from the vapour density of the gaseous element is 200, while the atomic weight deduced from Dulong and Petit's Law is also 200; we have then

$$200 = \frac{200}{N}$$

and therefore $N = 1$, or the molecule of mercury is **monatomic**. The molecules of zinc and cadmium, elements somewhat allied to mercury, are also monatomic.

ABNORMAL VAPOUR DENSITIES

Sulphur boils at about 444°C ., but the gaseous molecule subsequently undergoes interesting changes which seem to throw some light on this subject. Very near the boiling point the vapour density is 115, and therefore $M = 230$; from 468° to 606°

Biltz found that d varied from 113 to 68, and M , therefore, from 226 to 136. At nearly 800° , however, $d = 32$ and $M = 64$, and no further variation takes place.

Now the atomic weight of sulphur can be found from its gaseous compounds, sulphuretted hydrogen, sulphur dioxide, etc., as was that of carbon (page 41). It is found to be 32.

But if $32 = \frac{230}{N}$, N lies between 7 and 8 ;

while if $32 = \frac{136}{N}$, N lies between 4 and 5 ;

and if $32 = \frac{64}{N}$, $N = 2$.

The results more recently obtained by the application of Raoult's method to solutions of sulphur in carbon bisulphide, naphthalene, etc., leave little doubt as to the true explanation of the variations referred to. At the boiling point the molecule contains 8 atoms, and is represented by S_8 . Rise of temperature converts each 8-atom molecule into four 2-atom molecules, until at about 800° all have been so converted, and the permanent condition represented by S_2 is attained. The intermediate values of d represent mixtures, in varying proportions, of S_8 molecules with S_2 molecules. For instance, a mixture of 200 S_8 with 100 S_2 would have the same density as S_6 . This is about the composition in the neighbourhood of 500° , and the molecule used to be described as hexatomic on that account. Somewhat similar behaviour is shown by other substances, and even diatomic molecules may become monatomic. J_2 becomes I_1 . The conversion in this case seems to commence at about 700° , and to be complete at about $1,500^\circ$. It would seem probable, therefore, that the diatomic molecule is the rule simply because

the temperature at which more or less dissociation takes place does not fall, in the case of most elements, between the lower and higher limits of usual observation. **Exceptions occur** (1) when this temperature is **below the lower limit** of observation, and we find molecules monatomic when we first observe them—e.g. Hg, Zn, Cd, etc.; and (2) when this temperature is **above the higher limit**, and we find the molecules still consisting of more than 2 atoms—e.g. P_4 , As_4 , etc.

A similar phenomenon has been observed in the case of certain **compounds**, and of these nitrogen peroxide is a favourite example. At low temperatures $d = 46$, giving $M = 92$, and formula N_2O_4 at fairly high temperatures $d = 23$, giving $M = 46$ and formula NO_2 . At intermediate temperatures intermediate values are obtained due to varying mixtures of N_2O_4 and NO_2 , but further increase of temperature does not produce further variation. The higher, varying values of d are referred to, in these and similar cases, as **abnormal vapour densities**. Their occurrence is explained by the process described. It is called **dissociation**, and must not be confused with *decomposition*. The former process is, in a sense, reversible. The N_2O_4 , which by rise of temperature becomes $2NO_2$, will, as the temperature falls, be formed again by reunion of the two NO_2 molecules into one. Spontaneous reunion of the separated constituents does not take place after true *decomposition*.

EQUIVALENT WEIGHT

Elements vary both in atomic weight and in valency, and their exchange value is affected by both factors. In estimating this exchange value the hydrogen atom as usual serves as unit, and

we define the exchange value or *equivalent weight* * as **that weight of the element which can replace, or combine with, one part by weight of hydrogen.**

In the case of *monad* elements, one atom exchanges for *one* hydrogen atom, or the atomic weight is the equivalent weight; but in the case of *dyad* elements one atom exchanges for *two* hydrogen atoms, and therefore the atomic weight for *two* parts by weight of hydrogen. The atomic weight is therefore *twice* the equivalent weight, or

$$\text{Equivalent weight} = \frac{A}{2}$$

Similarly, in the case of *triad* elements we find

$$\text{Equivalent weight} = \frac{A}{3}$$

In fact, in all cases,

$$\text{Equivalent weight} = \frac{\text{atomic weight}}{\text{valency}}$$

An element can only have one atomic weight, but it may have several equivalent weights, because its valency may vary. Thus, the equivalent weight of iron in the ferrous salts is $\frac{56}{2} = 28$; in the ferric

salts, $\frac{56}{3} = 18.6$.

Equivalent weights are important, because they are the weights of elements and radicles which are liberated when an electric current is passed through a series of solutions. Thus, if we send a current through four vessels, containing respectively: (1) acidulated water; (2) salt solution, NaCl; (3) copper sulphate solution, CuSO₄; (4) gold cyanide solution

* It is often called the "chemical equivalent," and, more briefly, the "equivalent."

$\text{Au}(\text{CN})_3$; if 1 gram. of hydrogen is liberated in the first vessel, we shall have in the second 23 gram. of sodium and 35.5 gram. of chlorine, in the third $\frac{63.5}{2} = 31.75$ gram. of copper, and in the fourth $\frac{197}{3} = 65.7$ gram. of gold.

Determination of equivalents.—Equivalents can therefore be determined by finding the weight in grammes of an element liberated in the same time as 1 gram. of hydrogen. They are, however, often determined in the laboratory by simple chemical methods. A small weighed quantity of a metal—e.g. copper or zinc—is dissolved in nitric acid, the solution evaporated to dryness, and the dry residue strongly heated. In this way the oxide of the metal is obtained and weighed. We can now calculate what weight of the metal combines with 8 gram. of oxygen, and is therefore equivalent to 1 gram. of hydrogen.

CHAPTER IV

COMPOUNDS

Laws and Conditions of Chemical Combination — Law of Mass-Action — Classification and Nomenclature of Compounds—Acids, Bases, and Salts.

THE differences between a compound and a mixture, mentioned on page 7, are due to the fact that combination is regulated by definite laws.

LAWS OF CHEMICAL COMBINATION

The proportions by **weight** in which two elements combine are determined by the three following laws :—

1ST LAW. THE LAW OF CONSTANT PROPORTIONS

The same chemical compound always contains the same elements, united in the same proportions.

This law declares that a chemical compound always possesses an unvarying composition. For instance, from whatever part of the globe chloride of sodium (common salt) be obtained, or by whatever method it may be manufactured, it will always be found on analysis to contain 23 parts by weight of sodium to 35.5 parts by weight of chlorine, and these proportions will never vary in the compound. Again, if pure water be obtained from any source, and analysed, it will be found to contain 2 parts by weight of hydrogen to 16 parts by weight of oxygen, and in all samples of water these proportions are invariable.

This law, although a very simple one, is extremely important, for it confers on chemistry the dignity of an exact science. If this law were not true, we could not assign a formula to any compound.

2ND LAW. THE LAW OF MULTIPLE PROPORTIONS

When two elements A and B unite to form several compounds, the various weights of B which combine with a fixed weight of A are simple multiples of the smallest weight of B so combining.

The two oxides of carbon illustrate this law. In one, 100 parts by weight of carbon are combined with $133\frac{1}{3}$ parts of oxygen, in the other with $266\frac{2}{3}$ parts of oxygen; now $133\frac{1}{3} : 266\frac{2}{3} :: 1 : 2$, and the formulæ are CO and CO₂. Again, in the five compounds of nitrogen with oxygen, the various weights of oxygen combined with 100 parts by weight of nitrogen are 57, 114, 171, 228, 285. It is obvious that these various weights of oxygen are as 1 : 2 : 3 : 4 : 5.

This second law of chemical combination is an extremely important one, which adds great weight to the idea of the existence of atoms; for, since an atom is supposed to be indivisible, it is easy to understand why, in cases where several compounds of the same elements exist, the increase is always in some simple multiple of the combining weight: in other words, there is no halving nor quartering of atoms; in fact, the theory of the existence of atoms is perfectly in harmony with the law of multiple proportions that has just been explained.

It is owing to this law that we only require a symbol to represent one particular weight of the element, as already mentioned.

The discovery of the second law, the law of multiple proportions, by Dalton in 1804, was of the highest

importance; before Dalton's time the composition of a substance was expressed in percentage numbers. Thus the two oxides of carbon:

Carbonic oxide, 42·86 p.c. carbon and 57·14 p.c. oxygen.

Carbon dioxide, 27·27 p.c. carbon and 72·73 p.c. oxygen.

And again, two of the hydrocarbons:

Olefiant gas, 85·7 p.c. carbon and 14·3 p.c. hydrogen.

Marsh gas, 75·0 p.c. carbon and 25·0 p.c. hydrogen.

This method of expressing the composition does not disclose the really interesting relation between the compounds compared. For this purpose what we want to see is, not the composition of the *same* weight of every compound, but the composition of *different* weights of each compound, all containing the same weight of the same element.

Dalton was apparently the first to notice that in olefiant gas *one* part of hydrogen was united to *six* parts by weight of carbon, and that in marsh gas *two* of hydrogen were united to *six* parts of carbon, and *to appreciate the importance of this fact*. The most convenient "different weights" to choose are the *molecular weights*. The relations are then most obvious. Although the conception of the law is due to the penetrating insight of Dalton, the experiments by which its truth was established are mainly the patient and accurate work of Berzelius.

3RD LAW. THE LAW OF RECIPROCAL PROPORTIONS

The proportions in which any two elements unite with a third are the same proportions in which they unite with each other, or simple multiples of those proportions.

For instance, in carbon dioxide 12 parts of carbon combine with 32 parts of oxygen, and in methane

12 parts of carbon combine with 4 parts of hydrogen ; if hydrogen and oxygen combine they should, in accordance with this law, combine in the proportions of 4 : 32, or in simple multiples thereof. These are, as a matter of fact, the *same* proportions as occur in water (page 115).

The proportions by **volume** in which two elements unite, in the **gaseous** state, obey the following law :—

LAW OF VOLUMES OF GAY-LUSSAC AND HUMBOLDT

There is a simple relation between the volumes of gases which combine to form a chemical compound, and a similar simple relation exists between the volumes of the combining gases and that of the resulting gaseous compound.

Thus one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrogen chloride. Two volumes of hydrogen unite with one volume of oxygen to form two volumes of steam. One volume of nitrogen unites with three volumes of hydrogen to form two volumes of ammonia. In these examples the simplicity of the volumes combining is evident—1 : 1, 1 : 2, 1 : 3, and in all cases two volumes are formed. It follows from the above that the **WEIGHTS OF EQUAL VOLUMES OF ALL GASES ARE PROPORTIONAL TO THEIR COMBINING WEIGHTS, OR ARE A SIMPLE MULTIPLE THEREOF.**

THE LAW OF MASS-ACTION

Not only are chemical combinations regulated by the foregoing **laws**, but all chemical action is profoundly influenced by some of the **conditions** under which it occurs. The same two substances may react quite differently when present in different proportions and at different temperatures. Illus-

trations of this will be found later in the action of sulphuric acid on alcohol.

Most reactions, indeed, if allowed to run their natural course, tend to produce a condition of stable equilibrium dependent mainly on the two factors referred to. The law of mass-action defines this condition as follows. If p gramme molecules of

a substance	A present in concentration *				a
react with	q of B	„	„	„	b
and produce	r .. C	„	„	„	c
and	s .. D	„	„	„	d

Then the ratio

$$\frac{a^p \cdot b^q}{c^r \cdot d^s} = \text{a constant } k \text{ at a given temperature.}$$

CLASSIFICATION AND NOMENCLATURE OF COMPOUNDS

The compounds that are formed according to these laws are conveniently arranged in certain classes. When only *two* elements unite, the class of the resulting compound is named by adding the suffix **-ide** to the stem of the name of the more negative element. Thus, when an element combines

with chlorine	the compound is a chloride .			
„ bromine	„	„	a bromide .	
„ iodine	„	„	an iodide .	
„ oxygen	„	„	an oxide .	
„ sulphur	„	„	a sulphide .	

As compound radicles (page 26) function as elements, we also call $(\text{NH}_4)\text{—Cl}$ ammonium *chloride* and K—(CN) potassium *cyanide*.

* The “concentration” means the mass of substance per unit of volume.

To construct the correct formula of a chloride we require to know

1. The formula of hydrogen chloride, HCl ; and
2. The valency of the element which is to be substituted for hydrogen.

If we want the formula of silver chloride, we know that the symbol of silver (valency included) is Ag^{i} , and that it replaces hydrogen, atom for atom.

\therefore the formula is AgCl .

And similarly for any **monad** metal, M^{i} , it will be $\text{M}^{\text{i}}\text{Cl}$; but for any **dyad** metal M^{ii} , we must remember that M^{ii} must replace *two* atoms of hydrogen; we must therefore *double* HCl , and start, as it were, with H_2Cl_2 , giving, after replacement, $\text{M}^{\text{ii}}\text{Cl}_2$, which is the formula required—e.g. calcium chloride, $\text{Ca}^{\text{ii}}\text{Cl}_2$.

Similarly for a **triad** metal, M^{iii} , we first *treble* HCl , and then from H_3Cl_3 derive $\text{M}^{\text{iii}}\text{Cl}_3$ by suitable replacement.—e.g. aluminium chloride $\text{Al}^{\text{iii}}\text{Cl}_3$. An element which shows plural valency will have more than one chloride; thus iron forms two chlorides, $\text{Fe}^{\text{ii}}\text{Cl}_2$ and $\text{Fe}^{\text{iii}}\text{Cl}_3$; and mercury forms two, $\text{Hg}^{\text{i}}\text{Cl}$ and $\text{Hg}^{\text{ii}}\text{Cl}_2$. The names iron chloride and mercury chloride would therefore be not sufficiently definite. In cases of this kind the suffix **-ous** is used to denote the compound in which the *lower* valency is exercised, while the suffix **-ic** is reserved for the *higher* valency compound. Thus—

$\text{Fe}^{\text{ii}}\text{Cl}_2$ is Ferr-**ous** Chloride.

$\text{Fe}^{\text{iii}}\text{Cl}_3$ „ Ferr-**ic** „

$\text{Hg}^{\text{i}}\text{Cl}$ „ Mercur-**ous** „ (calomel).

$\text{Hg}^{\text{ii}}\text{Cl}_2$ „ Mercur-**ic** „ (corrosive sublimate)

$\text{P}^{\text{iii}}\text{Cl}_3$ „ Phosphor-**ous** „

$\text{P}^{\text{v}}\text{Cl}_5$ „ Phosphor-**ic** „

$\text{Sn}^{\text{ii}}\text{Cl}_2$ „ Stann-**ous** „

$\text{Sn}^{\text{iv}}\text{Cl}_4$ „ Stann-**ic** „

The formulæ of all bromides and iodides exactly

resemble those of the corresponding chlorides, Br or I being substituted for Cl. They will therefore present no difficulty.

To construct the formulæ of oxides, we begin with water, the best-known oxide of hydrogen, H_2O , and we can easily replace the hydrogen in this by two **monad** atoms or by one **dyad** atom :—

Ex.—Silver oxide, $\text{Ag}_2^{\text{i}}\text{O}$,
 Calcium oxide, $\text{Ca}^{\text{ii}}\text{O}$,
 (quicklime) ;

but for a **triad** we must treble H_2O , and in H_6O_3 replace the six atoms of hydrogen by two triad atoms :—

Ex.—Ferr-**ic** oxide, $\text{Fe}^{\text{iii}}_2\text{O}_3$
 Alumina, $\text{Al}^{\text{iii}}_2\text{O}_3$
 Arseni-**ous** anhydride, $\text{As}^{\text{iii}}_2\text{O}_3$
 (white arsenic).

A **tetrad** atom replaces *four* hydrogen atoms, and therefore we double H_2O , and from H_4O_2 obtain, for instance,

Stann-**ic** oxide, $\text{Sn}^{\text{iv}}\text{O}_2$.

A **pentad** atom can only replace hydrogen atoms, *five* at a time, so we must take five times H_2O , and from H_{10}O_5 obtain, for instance,

Phosphoric anhydride, $\text{P}^{\text{v}}_2\text{O}_5$.

A **hexad** atom replaces six hydrogen atoms, which are obtained by trebling H_2O , and the H_6O_3 becomes, say,

Sulphuric anhydride, $\text{S}^{\text{vi}}\text{O}_3$.

A **heptad** atom requires seven times H_2O , or H_{14}O_7 , from which we can derive, for example,

Permanganic anhydride $\text{Mn}^{\text{vii}}_2\text{O}_7$.

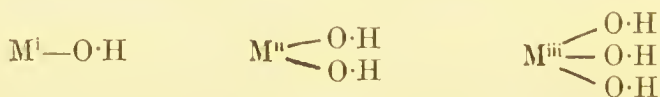
An **octad** atom requires four times H_2O , or H_8O_4 , from which is derived, for instance,

Perosmic anhydride, $\text{Os}^{\text{viii}}\text{O}_4$.

INTRODUCTION TO CHEMISTRY [PART I

Sulphides are derived from H_2S , and their formulæ only differ from those of the corresponding oxides in the fact that the symbol S replaces O. They will therefore present no difficulty.

Hydroxides form another very important class. They are compounds of an element (or compound radicle) with the monad compound radicle, hydroxyl, $-\text{O}-\text{H}$ or $(\text{OH})^i$. Water may be regarded as $\text{H}-\text{OH}$, hydrogen hydroxide, and the other hydroxides may be derived from it just as the chlorides were derived from HCl , hydrogen chloride. Their formulæ will therefore be exactly the same as those of the chlorides (page 54), except that Cl will be replaced by the group OH. They are therefore M^iOH , $\text{M}^{ii}(\text{OH})_2$, $\text{M}^{iii}(\text{OH})_3$, etc., or, graphically,



And so on. They will be fully illustrated as we proceed.

The compounds described in this section are also called **hydrates**. As the use of two different names for the *same* thing often confuses the student, an attempt has been made in the present edition to use the two different terms for different purposes. Hydroxide is used to denote the definite compounds, with definite formulæ, such as have just been described. Besides these definite compounds, however, there exist bodies of somewhat indefinite composition to which the term hydrate may be usefully applied. These include *moist oxides*—oxides more or less loosely united with varying proportions of water—and also certain aqueous solutions of substances, such as the solution of ammonia employed as a reagent in the laboratory, and usually labelled ammonium hydrate. In this case also the name

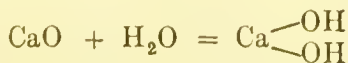
is appropriate, for the solution varies much in strength and composition, and is not known to contain a hydroxide of definite formula. It is now often denoted in chemical literature by the symbol $\text{NH}_3 \text{ Aq}$, in which NH_3 represents the definite compound, ammonia, and Aq the indefinite quantity of water (Latin *aqua*) in which the gas is dissolved. No doubt, in chemical reactions hydrates usually *play the part of hydroxides*. Indeed, in chemical equations they are often, on this account, represented by hydroxide formulæ. We may look upon them as *functional hydroxides*.

BASES, ACIDS, AND SALTS

Corresponding to the two types of elements—**positive** (metals) and **negative** (non-metals)—we recognise two types of hydroxides.

The hydroxides of the positive elements are **bases**, the hydroxides of the negative elements are **acids**. As positive element combines with negative, so also does base combine with acid; in the latter case the resulting compound is a **salt**. These three types of compound, base, acid, and salt, are of the greatest importance. Their history is, to a great extent, the history of chemistry. In order that the student may thoroughly understand them, each will very soon receive detailed consideration.

It will be convenient, however, to mention first that the difference in character between the two types of elements extends to their oxides also. The oxide of a positive element either dissolves in water and produces a *base*—



or, if not soluble in plain water, dissolves in water to which sufficient *acid* has been added, and then

behaves as a base by producing a salt. The oxides of positive elements are therefore called **basic** or **base-forming oxides**.

The oxide of a negative element either dissolves in water and produces an *acid*—



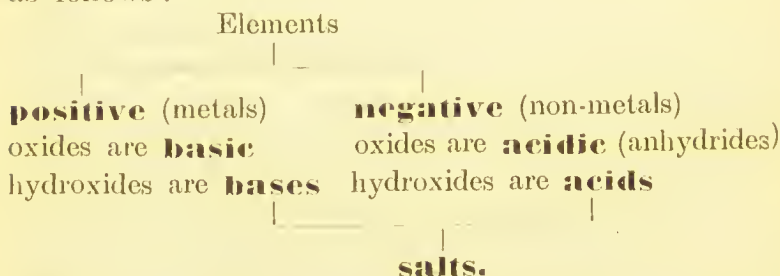
or, if not soluble in plain water, dissolves in water to which sufficient *base* has been added, and then *behaves as an acid by producing a salt*.

The oxides of negative elements are therefore called **acidic** or **acid-forming oxides**; they are also, and perhaps more frequently, termed **anhydrides**, from the fact, already illustrated, that they are, so to speak, the acids without water.

Ex.— SO_3 is sulphuric anhydride.

CO_2 is carbonic anhydride.

To enable the student to see more clearly the important relations indicated in this paragraph, the diagram presented on page 7 is now extended as follows:—



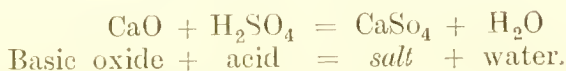
The detailed consideration of each class promised above (page 57) will now be proceeded with.

BASES

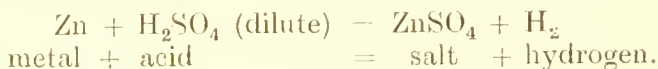
Scientific terms frequently tend, under the stress of practical use, to acquire a looser and more extended meaning than strictly belongs to them;

the term base illustrates this tendency, and is sometimes used to denote almost any substance that can, with the aid of an acid, produce a salt. So extended, the term includes:—

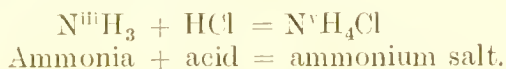
A basic oxide, as calcium oxide, for



A metallic element as zinc, for



Ammonia, or one of its numerous organic derivatives (amines, etc.), for



In these reactions each substance—calcium oxide, zinc, ammonia—does in turn undoubtedly *play the part of a base*, but we need not therefore call them bases; compound radicles *play the part of elements*, but they are not elements, and it would be wrong to call them so. None of the substances which here play the part of a base is a *hydroxide*, and the hydroxyl group is a significant feature of the true *base*. The other substances are functionally bases, but not structurally.

As the positive elements (and compound radicles) differ in *degree*, both as to valency and as to positive character, their hydroxides—the *bases*—must also differ in valency, and in the degree of their basic character. The strongest bases are those hydroxides of the monads, potassium and sodium; they are very soluble in water; the solution turns red litmus blue, has a soapy feel, and caustic properties. The divalent bases of calcium, barium, and magnesium are far less soluble in water, and the solutions obtained

exhibit similar properties, but are milder. The trivalent bases—e.g. aluminium hydroxide—are still less soluble, and still weaker in basic power.

ACIDS

The term acid has also acquired a more extended meaning, and often denotes "*any substance that contains hydrogen capable of being displaced by a metal and thus producing a salt.*" All the hydroxides of negative elements contain this typical hydrogen. But even if hydrogen alone—without oxygen—is *attached to a negative element*, it acquires this character. Thus the hydrogen associated with sulphur in H_2S can be so replaced, and this substance is sometimes called hydrosulphuric acid, although it is commonly known as *sulphuretted hydrogen* or *hydrogen sulphide*. It is, however, doubtful whether sulphides are any more entitled to rank as *salts* than oxides; and it must be borne in mind that if metallic sulphides are not *salts*, hydrogen sulphide is not an *acid*, and vice versa. The hydrogen associated with one of the strongly negative halogen elements, chlorine, bromine, iodine, also acquires the typical acid character, and it cannot be denied that HCl , HBr , HI *function as acids*, and they are commonly known as *hydrochloric acid*, *hydrobromic acid*, and *hydroiodic acid*.

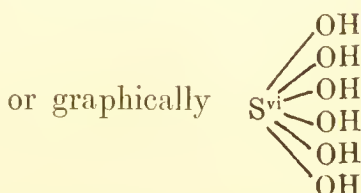
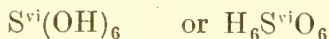
It still remains true, however, that the large majority of our acids are either hydroxides of negative elements (inorganic acids), or of negative compound radicals (organic acids), or direct derivatives of these. To distinguish them from functional acids of a different structure the inorganic ones are sometimes called *oxyacids*, the organic, *carboxylic acids*.

As negative elements differ in degree, both as to valency and as to negative character, their hydroxides—these *oxyacids*—must also differ in valency and

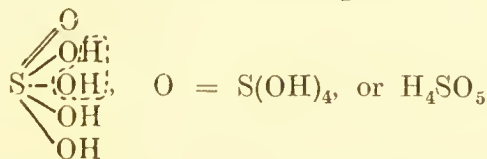
in the degree of their acid character. The valency of the negative element determines the number of hydroxyl groups attached to the element in the hydroxide.

It often happens, however, that no hydroxide with the full theoretical number of hydroxyl groups is known to exist, for **when two or more hydroxyl groups are attached to the same atom they tend to react with each other and form a water molecule, H_2O , which becomes independent.**

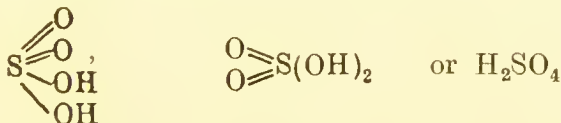
Thus the sulphur atom is hexad, and its proper hydroxide is



Owing to the tendency described, we may suppose this to become, by loss of one H_2O molecule, first,

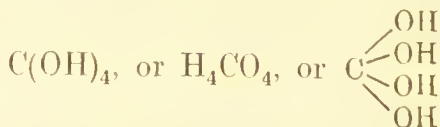


And, secondly, by loss of another H_2O molecule,

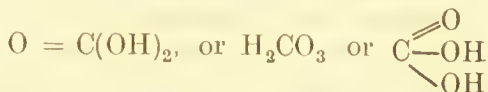


Neither H_6SO_6 nor H_4SO_5 is known, but H_2SO_4 is sulphuric acid—a common and very important member of the class. The *two* surviving hydrogen atoms are both capable of being replaced by a metal, and the acid is therefore said to be **dibasic**.

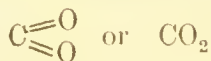
Similarly, the tetrad **carbon** should give rise to



which by loss of one H_2O would become



and by loss of another H_2O

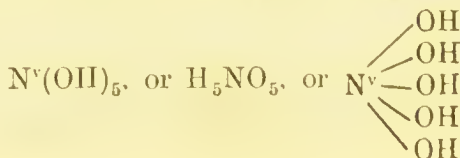


H_4CO_4 is not known, but organic salts of it are known; it is named *orthocarbonic acid*, and its salts orthocarbonates. H_2CO_3 has also not been isolated, but its inorganic salts—the carbonates—are numerous and familiar; it is *carbonic acid*.

CO_2 , though often called “carbonic acid,” has no right to the name. It contains no hydrogen at all, and therefore cannot contain the typical replaceable hydrogen *which every acid must contain*. It may be called carbon dioxide, or, preferably, *carbonic anhydride*.

The tetrad element **silicon** resembles carbon in many respects, and should provide two corresponding *silicic acids*, H_4SiO_4 and H_2SiO_3 , as well as a corresponding anhydride SiO_2 (silica). The anhydride is well known (*see* page 214), but it is doubtful whether either acid has been isolated in a pure state.

Similarly the full hydroxide of the pentad **nitrogen**,



becomes in this way $\begin{array}{c} \text{O} \\ \parallel \\ \text{N} \begin{array}{l} \nearrow \text{OH} \\ \searrow \text{OH} \\ \searrow \text{OH} \end{array} \end{array}$ or H_3NO_4

and finally $\begin{array}{c} \text{O} \\ \parallel \\ \text{N} \begin{array}{l} \searrow \text{O} \\ \searrow \text{OH} \end{array} \end{array}$ or HNO_3 .

Neither H_5NO_5 nor H_3NO_4 is known to exist, but HNO_3 is the well-known **nitric acid**. It has the structure here sketched, and is evidently **mono-basic**. Its salts are the *nitrates*.

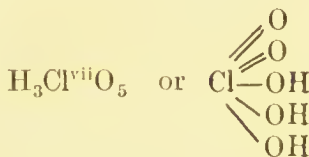
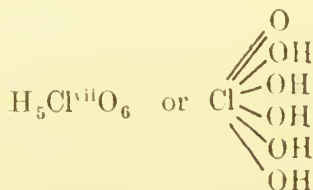
Phosphorus, another pentad element, resembles nitrogen, and will now present no difficulty. In this case, however, only H_5PO_5 is not known; both H_3PO_4 , *orthophosphoric acid*, and HPO_3 , *metaphosphoric acid*, exist, and are important acids. Hitherto our examples have shown the element employing its *maximum* valency, but we already know that this is not always the case, and the other cases deserve consideration here. **Sulphur**, for instance, may function as a **tetrad** like carbon, and therefore give rise to corresponding compounds—e.g. $\text{H}_4\text{S}^{\text{iv}}\text{O}_4$, $\text{H}_2\text{S}^{\text{iv}}\text{O}_3$, $\text{S}^{\text{iv}}\text{O}_2$. The first is not known to exist; $\text{H}_2\text{S}^{\text{iv}}\text{O}_3$ has not been isolated, but its salts (*sulphites*) are well known, and the acid is called *sulphurous acid*. SO_2 is a well-known gas, and is called *sulphurous anhydride*.

In these cases, as explained on page 54, we use the suffix **-ous** to distinguish the acid in which the lower valency is exercised, and **-ic** when the higher valency is used. The salts of **-ic** acids are called **-ates**; those of **-ous** acids are called **-ites**. Nitrogen, again, may function as a *triad*, and so begin with $\text{H}_3\text{N}^{\text{iii}}\text{O}_3$, leading by loss of H_2O to $\text{HN}^{\text{iii}}\text{O}_2$. H_3NO_3 is not known, but HNO_2 is *nitrous acid*, and its salts are *nitrites*. Its graphic formula

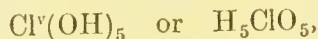
is therefore $\begin{array}{c} \text{O} \\ \parallel \\ \text{N}^{\text{iii}} \searrow \text{OH} \end{array}$

Phosphorus, again, resembles nitrogen, for it also functions as a *triad*, and thus produces $\text{H}_3\text{P}^{\text{iii}}\text{O}_3$, which in this case is known and is called *phosphorous acid*, and its salts are *phosphites*.

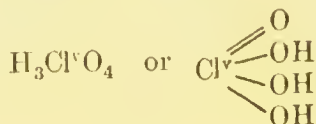
We have now indicated the origin and structure of most of the acids with which the student will be concerned, but the **oxyacids of chlorine** remain to be mentioned. **Chlorine** is a **heptad** element, and, if exerting its maximum valency, will have a hydroxide $\text{Cl}^{\text{vii}}(\text{OH})_7$, or H_7ClO_7 , which, by gradual loss of H_2O molecules as usual, will give rise in turn to the following compounds—

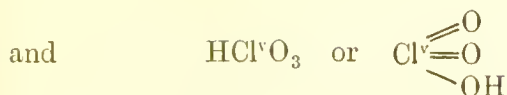


But chlorine may function as a *pentad*, and in that case the initial hydroxide will be



and this will lead in turn to





Again, chlorine may function as a *triad*, and begin with a hydroxide, $\text{H}_3\text{Cl}^{\text{iii}}\text{O}_3$, which will lead



or finally chlorine may function as a *monad*, and form only $\text{Cl}^{\text{i}}-\text{OH}$. Of these acids, $\text{HCl}^{\text{vii}}\text{O}_4$ has been obtained, several salts of $\text{HCl}^{\text{v}}\text{O}_3$, a few of $\text{HCl}^{\text{iii}}\text{O}_2$, and one, at least, of $\text{HCl}^{\text{i}}\text{O}$. We have therefore to distinguish these *four* acids; but our suffixes **-ous** and **-ic** only enable us to distinguish *two*. In this case $\text{HCl}^{\text{v}}\text{O}_3$ is called ehlor-*ic* acid, and $\text{HCl}^{\text{iii}}\text{O}_2$ is ehlor-*ous* acid. There now remain $\text{HCl}^{\text{vii}}\text{O}_4$, in which the valency of Cl is *above* that in ehloric acid, and this is therefore named **perchloric** acid (Latin, *super*, above), as well as $\text{HCl}^{\text{i}}\text{O}$, in which the valency is *under* that in ehlorous, and this is therefore named **hypochlorous** acid (Greek, *ὑπό*, under).

The salts are named *perchlorates*, *ehlorates*, *chlorites*, and *hypochlorites*. Their stability diminishes with the valency exercised by the chlorine atom, perchlorates being the most stable and hypochlorites the least. This is an interesting illustration of the general rule that saturated compounds are more stable than unsaturated ones of kindred structure.

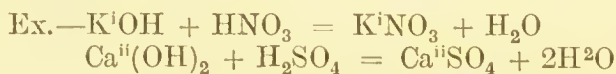
SALTS

A salt may evidently be defined as the compound which results from chemical action between a base and an acid. This action consists essentially in the formation of H_2O by the combination of the typical H of the acid with the OH group of the base; at

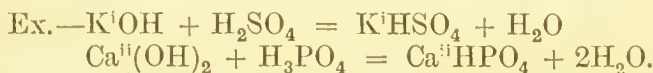
the same time the positive element of the base replaces the typical H in the acid to form the salt.

There will, however, be **three different classes of salts** owing to the fact that bases and acids both vary in valency. These three classes must now be named and discussed.

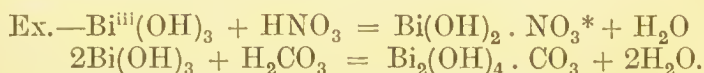
1. **Normal salts.**—These are formed when the valency of the base is **equal** to the basicity of the acid; that is to say, when the number of OH groups of the base is equal to the number of typical H atoms of the acid.



2. **Acid salts.**—These are formed when the valency of the base is **less** than the basicity of the acid.



3. **Basic salts.**—These are formed when the valency of the base is **greater** than the basicity of the acid.

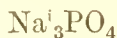
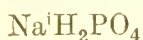


Formulae of salts.—When the formula of an acid is known, the formulae of its salts can be derived by the methods already illustrated (pages 54, 56). Just as we obtained the formulae of all other chlorides from that of hydrogen chloride, HCl, so we obtain the formulae of all nitrates from that of hydrogen nitrate, HNO_3 ; in fact, NO_3 occurs in place of Cl. Similarly the formulae of sulphates are obtained from

* The tendency to elimination of H_2O from two OH groups attached to the *same* atom, which has been already mentioned (page 61), prevails in these compounds also, and leads in their case to $\text{BiO} \cdot \text{NO}_3$ and $\text{Bi}_2\text{O}_2 \cdot \text{CO}_3$, the oxynitrate and oxycarbonate of bismuth employed in medicine.

H_2SO_4 , just as the formulæ of oxides were obtained from H_2O ; SO_4 now occurs in place of O. The student should find no difficulty in constructing the formula of any salt of a monobasic or dibasic acid. He will, however, sometimes require the formulæ of salts of a **tribasic** acid such as H_3PO_4 , and as this seems often to present more difficulty to beginners (for whom this book is more especially written), it will now be explained.

The orthophosphates of a monad metal such as sodium Na^i will evidently be represented by the three formulæ:



All exist, but the second is the common sodium phosphate employed in medicine; an aqueous solution of it is one of the laboratory reagents. Three orthophosphates of a *dyad* metal, such as calcium, are also possible, but their formulæ are not quite so easily obtained, because in this case the *dyad* atom can only replace the typical H atoms, *two at a time*. From H_3PO_4 we can therefore only obtain $\text{Ca}^{ii}\text{HPO}_4$; to obtain the other salts we must double H_3PO_4 , and from the $\text{H}_6(\text{PO}_4)_2$ so obtained we easily derive $\text{Ca}^{ii}_3(\text{PO}_4)_2$, the normal phosphate used in medicine and the chief mineral constituent of our bones; and also $\text{CaH}_4(\text{PO}_4)_2$, a much more soluble salt.

The *normal* phosphate of a *triad* metal like iron is easily formed from H_3PO_4 , since a triad atom can replace the H atoms *three at a time*. Iron will therefore form *two* normal phosphates:



Both are present in the "iron phosphate" used in medicine.

It may be convenient to mention here that the

typical H atoms of an acid may sometimes be replaced partly by *one* element or compound radicle, and partly by *another*, giving rise to a sort of *mixed salt*. Two phosphates of this type deserve notice and will be referred to later; they are "micro-cosmic salt," $\text{Na}(\text{NH}_4)\text{HPO}_4$ (page 279), and $\text{Mg}^{\text{it}}(\text{NH}_4)\text{PO}_4$ (page 298).

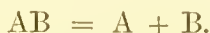
CHAPTER V

CHEMICAL REACTIONS

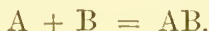
General Classes—Special Classes—Action of Acids on Metals—Oxidation and Reduction—Catalytic Reactions—Reversible Reactions.

THE student has already learned (page 16) that chemical changes are mainly effected by two processes, analysis and synthesis. These may operate singly, or in combination. A large number of chemical reactions are accordingly classified under one or other of the following heads. In each case a typical diagrammatic equation illustrates the kind of action taking place.

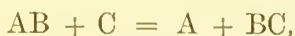
I. ANALYSIS :



II. SYNTHESIS :



III. SINGLE DECOMPOSITION :



or



IV. DOUBLE DECOMPOSITION :



or



Processes III. and IV. are evidently mere combinations of I. and II. AB and CD are decomposed by I., and from the separated units new compounds, AC, BC, etc., are formed by II.

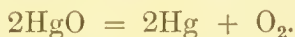
Examples of equations that illustrate these four types will now be considered :—

I. ANALYSIS (typical equation $AB = A + B$).—Under this head will come those equations which represent the splitting up of a compound body into its elements, or into less complex bodies.

1. When mercuric oxide is heated, it splits up into its elements, mercury and oxygen :

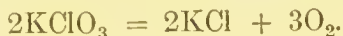


This equation, however, only represents an *instantaneous* state of things. The symbol O represents an *atom* of oxygen, and it has already been stated (page 27) that an atom cannot, in general, preserve an independent existence for a measurable time. This privilege belongs to the molecule, which usually contains, as we have seen, at least *two* atoms. We must, therefore, represent two molecules of mercuric oxide in the equation, which will then produce a molecule of free oxygen (O_2) which is capable of existing in the free state, thus :



The number is placed before the Hg to represent two molecules of mercury, for mercury is one of the exceptional elements that have monatomic molecules (page 44). Our equation is intended to represent the permanent *result* of the change rather than the actual process by which that result is attained. The student must therefore remember to represent the existence of molecules in equations, which will accordingly often have to be doubled, as in the case of the one just given.

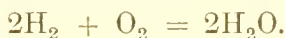
2. The next equation represents the manner in which chlorate of potassium (KClO_3) splits up, when heated, into chloride of potassium and oxygen :



The equation $\text{KClO}_3 = \text{KCl} + 3\text{O}$ would not be correct since it represents the formation of a molecule and a half of oxygen, and half a molecule is incapable of a free existence. The large number 2 placed before the KClO_3 multiplies everything after it as far as the sign $=$; the small $_3$ placed under the O is therefore multiplied by the large 2.

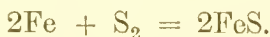
II. SYNTHESIS (typical equation $\text{A} + \text{B} = \text{AB}$).
—Equations of this kind represent the combination together of elements to form compounds, and also the combination of simple compounds to form more complex compounds.

1. The following equation represents the formation of water by the combination of hydrogen with oxygen:

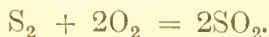


The equation $\text{H}_2 + \text{O} = \text{H}_2\text{O}$ would not be correct, as O represents an atom of oxygen which cannot exist in the free state (it will not be necessary to explain again why, in equations similar to this, the double number is used (*see* page 70)).

2. The next equation represents the formation of sulphide of iron (FeS) by the union of iron and sulphur (which can be effected by means of heat):



3. The following equation represents the formation of sulphur dioxide (SO_2) by the combustion of sulphur in oxygen:



III. SINGLE DECOMPOSITION (typical equations $\text{AB} + \text{C} = \text{A} + \text{BC}$ and $\text{AB} + \text{C} = \text{AC} + \text{B}$).
—The student will meet with numerous equations of this kind in the study of Chemistry. The following are a few examples:—

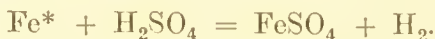
1. The action of zinc on hydrochloric acid (HCl),

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when chloride of zinc (ZnCl_2) is formed and hydrogen set free :



2. The action of iron on dilute sulphuric acid (H_2SO_4), when sulphate of iron (FeSO_4) is formed and hydrogen set free :



3. The reduction of oxide of copper (CuO) to the metallic state by means of charecoal, a decomposition that is effected by heating the two together, when the carbon abstracts the oxygen, forming carbon dioxide (CO_2) :



4. The formation of reduced iron (finely-divided iron), by passing hydrogen over heated ferric oxide (Fe_2O_3), when the hydrogen abstracts the oxygen, with the formation of water and free iron :



In this equation it is necessary to take 3H_2 in order to furnish sufficient hydrogen to unite with the three atoms of oxygen contained in the Fe_2O_3 .

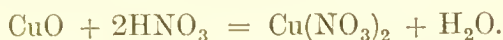
IV. DOUBLE DECOMPOSITION (typical equations $\text{AB} + \text{CD} = \text{AC} + \text{BD}$ and $\text{AB} + \text{CD} = \text{AD} + \text{BC}$).—Equations of this class are the most general that the student will meet with, reactions of double decomposition being of very common occurrence. The following examples are of general interest :—

1. When an oxide of a metal dissolves in an acid, as a rule, double decomposition takes place, the metal of the oxide uniting with the acid radicle of

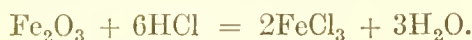
* The molecular weight of iron is not yet known. Moreover, when an element in the solid state takes part in a reaction, it is often represented by the symbol only.

the acid to form a salt, and the oxygen of the oxide uniting in its turn with the hydrogen of the acid to form water. Such oxides are basic oxides, and in this reaction they function as bases. This has already been explained and exemplified (page 58), but two further examples are now added :

(a) Equation representing the action of nitric acid (HNO_3) on oxide of copper (CuO) :



(b) Equation representing the action of hydrochloric acid (HCl) on ferric oxide (Fe_2O_3) :



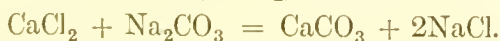
2. The formation of a salt by the reaction between a base and an acid is another example of double decomposition. It has already been described and illustrated (page 66).

3. When solutions of two soluble salts are mixed together and an insoluble salt called the *precipitate* is produced, the reaction is generally one of double decomposition ; thus :

(a) Equation representing the precipitation of sulphate of barium (BaSO_4) by adding sulphuric acid (H_2SO_4) to solution of chloride of barium (BaCl_2) :



(b) Equation representing the precipitation of carbonate of calcium (CaCO_3) by the addition of solution of carbonate of sodium (Na_2CO_3) to solution of chloride of calcium (CaCl_2) :



(c) Equation representing the precipitation of mercuric iodide (HgI_2) by the addition of solution of iodide of potassium (KI) to solution of mercuric chloride (HgCl_2) :



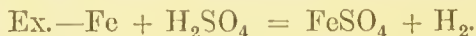
ACTION OF ACIDS ON METALS

The action of acids on metals can also be stated in somewhat general terms. For this purpose most of the metals which are of interest to the student of medicine may conveniently be divided into two groups. One group (A) includes silver, lead, mercury, bismuth, and copper; the other group (B) includes iron, aluminium, zinc, manganese, barium, calcium, magnesium, potassium, and sodium.

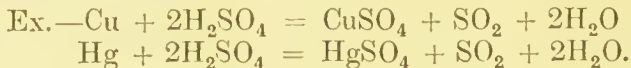
Hydrochloric acid solution, strong or dilute, has no appreciable action on a member of group A, but readily dissolves any member of group B, with evolution of hydrogen and formation of the metallic chloride. If the metal has two chlorides it is the *-ous* chloride which is formed in this reaction.



Sulphuric acid, dilute, has no appreciable action on an A metal, but readily dissolves a B metal, with evolution of hydrogen and formation of the metallic sulphate. If the metal has two sulphates it is the *-ous* salt which is formed.



Sulphuric acid, strong, does, with the aid of heat, dissolve an A metal, with evolution of sulphur dioxide and formation of the metallic sulphate.

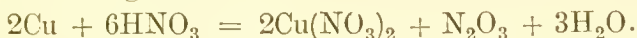


Strong sulphuric acid acts similarly on the B metals, but, as they are dissolved by the dilute acid, the reaction is of no practical use in their case.

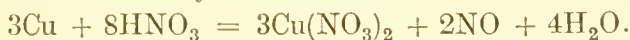
Nitric acid acts on members of either group in much the same way, with the exception of aluminium, which is not affected by this acid, strong or dilute, and of iron, which is not appreciably affected by

the *strong* acid. With these exceptions the action generally results in the formation of a metallic nitrate, and the evolution of one or more of the oxides of nitrogen. Some *reduction* (page 76) of the acid therefore takes place; indeed, ammonium salts are sometimes among the by-products. The course of the reaction is no doubt modified by the strength of the acid and by the temperature; the equations generally accepted express only the main features. With this caution they are now given in the typical case of copper.

With strong nitric acid



With moderately diluted nitric acid



The three elements, arsenic, antimony, and tin, show certain special features in their behaviour towards acids. **Arsenic** forms no nitrate or sulphate, but is converted, like a non-metal, into an acid or anhydride. **Antimony** also is mainly converted into oxide by strong nitric acid; it behaves, however, rather like an A metal with sulphuric acid, and forms a sort of sulphate. **Tin** behaves rather like a B metal, both with hydrochloric and sulphuric acid, and slowly forms the stannous salt in both cases. With dilute nitric acid it forms a nitrate, but by the strong acid the element is oxidised to an acid or anhydride.

Besides the *general* classes of reactions already described there are certain *special* classes which must now be considered.

REACTIONS RESULTING IN OXIDATION AND REDUCTIONS

On page 54 many examples were given of pairs of corresponding compounds in which the *same*

element exercised a higher valency in one of the pair than in the other. These were distinguished by means of the respective suffixes *-ic* and *-ous*. There are many reactions in which the significant feature is the conversion of an *-ic* compound into the corresponding *-ous* compound, or vice versa; or, in more general terms, the diminishing or increasing of the active valency of an element. **Any process whereby oxygen is added to a molecule, or the active valency of an element increased, is described as oxidation,** and any agent by which this result is effected is described as an **oxidising agent**. **Any process whereby oxygen is removed from a molecule, or the active valency of an element diminished, is described as reduction,** and any agent by which this result is effected is described as a **reducing agent**.

As each process is the converse of the other, the same reaction usually provides an illustration of both. For instance, when black copper oxide is mixed with a little powdered carbon and the mixture heated in a hard test-tube, carbonic anhydride is formed, and reddish particles of metallic copper are obtained :—



By this reaction the *active* valency of the copper is diminished from 2 to zero, while the *active* valency of the carbon is increased from zero to 4. The copper oxide has been *reduced* to metallic copper by the carbon, while the carbon has at the same time been *oxidised* to carbonic anhydride. Carbon is therefore a *reducing* agent and copper oxide an oxidising one. Instances of this kind were among the earliest illustrations of the processes, which therefore came naturally to be regarded as

consisting merely of the addition or removal of oxygen. Hence the name "oxidation," while "de-oxidation" is also used for "reduction." It is now commonly recognised that this view is too limited, and the student should be careful to adopt the more general one which has now been placed before him. Many more illustrations will be found in the text; the two following often serve as tests:—

1. The addition of an *oxidising agent* causes a blue colour to appear in an aqueous solution of potassium iodide which contains a few drops of starch solution and has been slightly acidulated with dilute sulphuric acid.

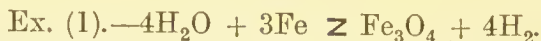
2. The addition of a *reducing agent* causes the red colour to disappear from an aqueous solution of potassium permanganate which has been acidulated with dilute sulphuric acid. (The test solution sometimes requires to be heated.)

CATALYTIC REACTIONS

Under this name are included all instances of chemical changes which are apparently *effected*, and are really *accelerated*, by the presence of some substance which does not itself suffer a permanent change. This phenomenon is called **catalysis** and the substance referred to is called a **catalytic agent**. The presence of platinum, for instance, promotes, in this way, the combination of hydrogen and oxygen to form H_2O , and also the combination of SO_2 and O to form SO_3 . Other instances will be mentioned later.

REVERSIBLE EQUATIONS

The symbol **Z** instead of $=$ is sometimes placed between the two parts of a chemical equation to indicate that the equation may be read either from left to right or from right to left, and will represent a real reaction in each case.



If steam is passed over strongly heated iron, it is reduced to hydrogen, and the iron is oxidised. The equation read from left to right represents this reaction. But if hydrogen is passed over strongly heated iron oxide, the oxide is reduced to the metal, and the hydrogen oxidised to steam. The truth is that both hydrogen and steam are present in both cases, but that in accordance with the law of mass-action (page 52) the proportion of hydrogen is relatively large at one temperature and the proportion of steam at another.



This equation also represents two reactions, and which of the two will take place really depends on the relative concentration of the HCl. Read from left to right, the HCl present is very much diluted; read from right to left, the HCl is strong. In our equations we use the same symbol, H_2O , for water, whether there is relatively much or little, and the same symbol for an acid, whether it is strong or dilute; we also omit to indicate the temperature at which the reaction takes place. If these omissions were rectified the apparent reversibility would practically disappear, and the equation would then become a more complete statement of the reaction.

It may be well to conclude this chapter with a word of warning to the student. He is often told to verify his equations by seeing that the number and nature of the atoms on one side are the same as those on the other, and he soon learns to apply this excellent test. Unfortunately, he does not so soon learn that an equation may satisfy this test, and therefore be quite correct *on paper*, but be altogether wrong in reality, because it represents a reaction which does not really occur. For instance, the equation

$\text{Cu} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2$ fulfils the required condition, and is frequently given by candidates in examination papers. It is, however, quite wrong, for it represents a fictitious reaction: Copper is *not* one of the metals included in group B (page 74), and hydrogen can *not* be obtained from copper, as it is from zinc. The student should therefore always try to satisfy himself not only that his equation balances in the way suggested, *but that it also represents a really possible reaction between the substances concerned.*

CHAPTER VI

THE PERIODIC CLASSIFICATION OF THE ELEMENTS

WE have already recognised two great classes of elements, and have distinguished them as *positive* or *negative* and as *metals* or *non-metals*. Reference has also been made (page 22) to the fact that the atoms of different elements differ both in weight and valency; but no hint was then given that these differences were in any way connected. A glance at the following common elements, however, will show that *growth in valency accompanies growth in atomic weight*.

Element.	Symbol.	Atomic Weight.	Maximum Valency.
Sodium	Na	23	i
Magnesium	Mg	24	ii
Aluminium	Al	27	iii
Silicon	Si	28	iv
Phosphorus	P	31	v
Sulphur	S	32	vi
Chlorine	Cl	35.5	vii

Sodium, the *first* of the seven, is a strongly positive element, while **chlorine**, the last, is strongly negative. The change of character is not abrupt; it is reached by gradual stages, represented by the intervening elements. Here, then, we find a gradual change in type accompanying the gradual change in atomic weight and in valency.

The element which immediately precedes sodium is **neon** (at. wt. 20). It is one of a group of closely related elements discovered by Sir William Ramsay. They are present in minute quantity in the atmosphere, but form no compounds, and seem almost devoid of chemical energy. Coming between the extremely positive sodium and the extremely negative fluorine (at. wt. 19), neon seems to mark a turning-point or "dead point" in the cycle of character change.

The seven elements *preceding* neon are :—

Element.			Symbol.	Atomic Weight.	Maximum Valency.
Lithium	Li	7	i
Beryllium	Be	9	ii
Boron	B	11	iii
Carbon	C	12	iv
Nitrogen	N	14	v
Oxygen	O	16	*
Fluorine	F	19	*

This set of seven shows the same striking relation as the other. There is the same gradual change in character from the strongly positive **lithium** to the most strongly negative **fluorine**. Again, rise in valency accompanies rise in atomic weight, at any rate for the first five elements. The maximum valency of **oxygen** should be six, but we know of no instance in which this is exerted; it commonly acts as a **dyad**. The maximum valency of **fluorine** should also be seven, but it must be admitted that it commonly acts as a **monad**.

In chemical and physical characters each member of one set closely resembles the *corresponding* member of the other set, thus :—

* Uncertain, *see* text.

Lithium	closely	resembles	sodium.
Beryllium	„	„	magnesium.
Boron	„	„	aluminium.
Carbon	„	„	silicon.
Nitrogen	„	„	phosphorus.
Oxygen	„	„	sulphur.
Fluorine	„	„	chlorine.

The recognition of these resemblances led John Newlands, in 1864, to point out that if the elements were arranged *in the numerical order of their atomic weights*, commencing with lithium, there was a recurrence of similar chemical and physical characters at every eighth element (“The Law of Octaves”).

Some five years afterwards this idea was more fully developed by Mendeléeff, who published a table of the elements arranged according to his “Periodic Law.” Since that time new elements have been discovered, and his table, with some modifications and additions, now appears in the form printed on page 88. The elements are there arranged, horizontally in twelve *series*, and vertically in eight *groups*.

The following points deserve notice:—

1. After the first two octaves (lithium to chlorine) the resemblance is most marked between alternate, rather than between consecutive, octaves. Thus, taking the second vertical column, magnesium, zinc, and cadmium form a natural group, and the other alternate octaves, calcium, strontium, and barium, form a second natural group. In the fifth column phosphorus, arsenic, and antimony, and in the seventh column chlorine, bromine, and iodine, illustrate the same point.

2. In the eighth column, neon and the members of the neon group find their places. In this column also instead of a *single* element a triplet occurs in at least three places. In each case the triplet consists of three closely allied elements with atomic

weights very nearly equal. The exact values, for instance, in the first triplet are believed to be:—

Iron	55.85.
Nickel	58.68.
Cobalt	58.97.

If, therefore, we adhered strictly to the numerical order of their atomic weights, we should leave iron in the eighth column and transfer nickel and cobalt to the first and second columns respectively of the next series. The properties of nickel and cobalt do not in the least fit them for these positions, and to install them there would displace elements which are at present in suitable positions and force them into quite unsuitable ones. Zinc, for instance, would be pushed from the second column to the fourth, arsenic from the fifth to the seventh, and bromine from the seventh to the first. The objections to such a distortion are insuperable, and the triplet is therefore retained in the eighth column. Similar arguments lead to a similar conclusion in the case of the other triplets.

3. The valency rises from one to eight as we pass from the first group to the eighth. This fact is illustrated by the formulæ of the oxides placed at the head of the columns. The valency towards hydrogen, however, is indefinite and uncertain in the early and more positive groups, but falls from four to one in the well-marked hydrides of the later and more negative groups, e.g. CH_4 , NH_3 , OH_2 , FH . This illustrates the *reciprocal* nature of valency to which reference has already been made (page 23).

It is evident that this classification greatly simplifies the study of inorganic chemistry, and reduces it, speaking broadly, to the study of eight types instead of some eighty elements. It has also done great service to chemistry in two other respects:

(a) In correcting or confirming the values of the atomic weights found by different methods. The equivalent weight of indium is 38, and its atomic weight was at one time believed to be $38 \times 2 = 76$; but as there is no space for an element between arsenic and selenium, it was suggested that its atomic weight was $38 \times 3 = 114$, which would place it in the column under aluminium. This number was afterwards confirmed by a determination of its specific heat.

(b) It enables us to prophesy the existence and the physical and chemical properties of undiscovered elements. Thus, in columns III. and IV., when the table was first published the elements gallium (Ga) and germanium (Ge) were unknown, but by comparing the properties of aluminium and indium in the one case, and of silicon and tin in the other, an accurate forecast of all the chief properties of these elements was made, which was completely verified when the elements were isolated.

The **periodic** character is more clearly shown when the relation between the atomic weight and some other selected property is represented graphically. This is done by marking off, along a horizontal line OX (Fig. 4), distances from O proportional to the atomic weights, and then, from each point so obtained, drawing a vertical line, parallel to OY, to represent by its length the value of the chosen property for each element. The line obtained by joining the upper extremities of these vertical lines is a graphic representation of the change in value of the chosen property which accompanies a change in the atomic weight.

The **atomic volume** is a property often selected for exemplification. For all masses, the product, volume \times specific gravity, is equal to the weight; therefore for *atoms*

atomic volume \times specific gravity = atomic weight,

$$\therefore \text{atomic volume} = \frac{\text{atomic weight}}{\text{specific gravity}}.$$

Ex.—Lithium, at. wt. = 7; spec. grav. (solid) = .588,

$$\therefore \text{atomic volume} = \frac{7}{.588} = 11.9.$$

Values so obtained have been used in Fig. 4, and the graph obtained shows very clearly the *periodic* character of this function of the atomic weight.

In presenting the curve the object has been to show clearly the general rise and fall in the value of the atomic volume for the elements considered. Values have therefore been chosen, where choice was possible, which serve this purpose best. Carbon, for instance, has a different specific gravity in each of its three forms (*see* page 198), and therefore will have a different atomic volume in each case. The value used here belongs to *graphite*. Phosphorus also presents a choice; the *red* variety has been chosen. Nitrogen belongs to a family where such variations are the rule rather than the exception, but only one form of solid nitrogen is known at present, and the value from that gives the element a higher position than the one, found by interpolation, on the main curve. Neon has been interpolated.

Curves have also been traced for melting-point and many other properties. All point to the same conclusion: that every property of an element is some function of its atomic weight; that the nature of an atom is therefore determined by its weight; that, in fact, the different atoms are not really different kinds of matter, but different proportions of some one kind of matter. We have not yet *arrived* at this conclusion, but few chemists will now be greatly surprised if attempts to effect the transmutation of elements should prove more successful in the future than they have been in the past.

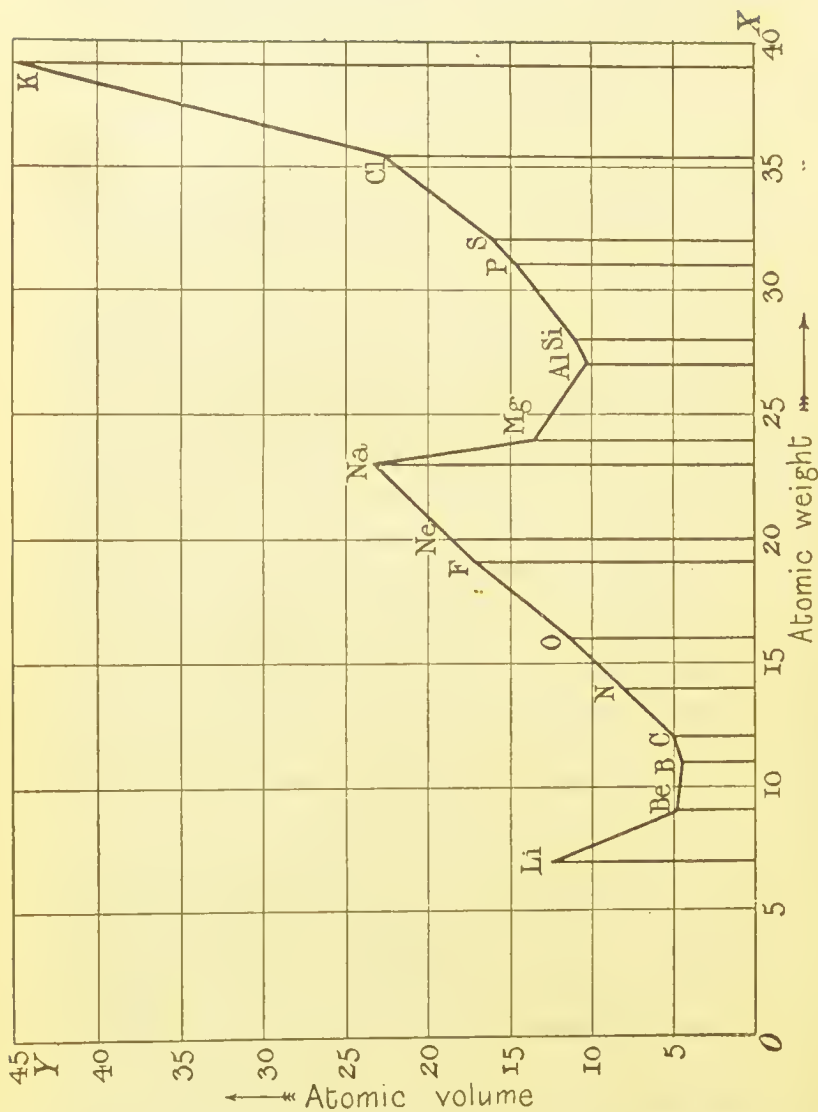


Fig. 4.—Graph showing the **periodic** character of the relation between atomic volumes and atomic weights for each of sixteen consecutive elements from lithium to potassium.

1910

International Atomic Weights

O = 16.		O = 16.	
Aluminium	Al 27.1	Molybdenum ...	Mo 96.0
Antimony	Sb 120.2	Neodymium ...	Nd 144.3
Argon	A 39.9	Neon	Ne 20.0
Arsenic	As 74.96	Nickel	Ni 58.68
Barium	Ba 137.37	Nitrogen	N 14.01
Bismuth	Bi 208.0	Osmium	Os 190.9
Boron	B 11.0	Oxygen	O 16.00
Bromine	Br 79.92	Palladium	Pd 106.7
Cadmium	Cd 112.40	Phosphorus ...	P 31.0
Cesium	Cs 132.81	Platinum	Pt 195.0
Calcium	Ca 40.09	Potassium	K 39.10
Carbon	C 12.00	Praseodymium	Pr 140.6
Cerium	Ce 140.25	Radium	Ra 226.4
Chlorine	Cl 35.46	Rhodium	Rh 102.9
Chromium	Cr 52.0	Rubidium	Rb 85.45
Cobalt	Co 58.97	Ruthenium	Ru 101.7
Columbium ...	Cb 93.5	Samarium	Sa 150.4
Copper	Cu 63.57	Scandium	Sc 44.1
Dysprosium ...	Dy 162.5	Selenium	Se 79.2
Erbium	Er 167.4	Silicon	Si 28.3
Europium	Eu 152.0	Silver	Ag 107.88
Fluorine	F 19.0	Sodium	Na 23.00
Gadolinium ...	Gd 157.3	Strontium	Sr 87.62
Gallium	Ga 69.9	Sulphur	S 32.07
Germanium ...	Ge 72.5	Tantalum	Ta 181.0
Glucinum	Gl 9.1	Tellurium	Te 127.5
Gold	An 197.2	Terbium	Tb 159.2
Helium	He 4.0	Thallium	Tl 204.0
Hydrogen	H 1.008	Thorium	Th 232.42
Indium	In 114.8	Thulium	Tm 168.5
Iodine	I 126.92	Tin	Sn 119.0
Iridium	Ir 193.1	Titanium	Ti 48.1
Iron	Fe 55.85	Tungsten	W 184.0
Krypton	Kr 83.0	Uranium	U 238.5
Lanthanum ...	La 139.0	Vanadium	V 51.2
Lead	Pb 207.10	Xenon	Xe 130.7
Lithium	Li 7.00	Ytterbium	
Lutecium	Lu 174.0	(Neoytterbium)	Yb 172.0
Magnesium	Mg 24.32	Yttrium	Y 89.0
Manganese	Mn 54.93	Zinc	Zn 65.37
Mercury	Hg 200.0	Zirconium	Zr 90.6

THE PERIODIC TABLE OF THE ELEMENTS (NEWLANDS AND MENDELÉEFF)

Group	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Typical Oxide	R_2O	RO	R_2O_3	RO_2	R_2O_3	RO_3	R_2O_7	RO_4
Series 1	H 1	—	—	—	—	—	—	He 4.
"	Li 7	Be†9	B 11	C 12	N 14	O 16	F 19	Ne 20.
"	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35.5 Cl	A 40.
"	K 39	Ca 40	Se 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56.
"	63.6 Cu	65.4 Zn	70 Ga	72.5 Ge	75 As	79 Se	80 Br	Co 59.
"	Rb 85.5	Sr 87.6	Y 89	Zr 90.6	Nb 94	Mo 96	—	Kr 83.
"	108 Ag	112 Cd	115 In	119 Sn	120 Sb	127.5* Te	—	Ru 102.
"	Cs 133	Ba 137.4	La 139	Ce 140	Pr 140.5	Nd 144	127 I	Rh 103.
"	157 Gd†	159 Tb†	162.5 Dy†	—	—	—	Sa 154.3	Xe 130.7.
"	—	Tm 168.5	Yb 172	Lu 174	167 Er	—	—	Eu 152.
"	197 Au	200 Hg	204 Tl	207 Pb	208 Bi	W 184	—	Os 191.
"	—	Ra 226.4	—	Th 232.5	—	U 238.5	—	Ir 193.
"	—	—	—	—	—	—	—	Pt 195.

* The atomic weight of tellurium still remains higher than that of iodine, but they are retained in what are undoubtedly their proper groups, pending further determinations. Argon and potassium afford a similar instance.

† This element is also known as Glucinum (Gl).

‡ The exact position of this element is still uncertain.

PART II.—INORGANIC CHEMISTRY : THE NON-METALLIC ELEMENTS

CHAPTER I

HYDROGEN

History—Preparation and Properties—Combustion—
Diffusion of Gases and Liquids—Graham's Law—
A Reducing Agent.

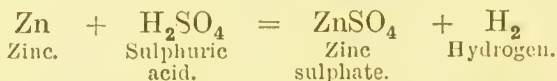
*Symbol, H ; molecule, H₂ ; monad ; atomic weight, 1 ;
molecular weight, 2 ; liquefies at -253° ; freezes
at -257° ; critical temperature about -243° .*

History.—Hydrogen exists in nature principally in combination with oxygen in the form of water, and it owes the derivation of its name (from *ὑδωρ*, water ; *γεννάω*, I produce) to the fact that when united with oxygen in certain proportions, it produces water.

In 1766 Cavendish recognised it as an “ inflammable air ” derived from metals. He obtained it from zinc and iron by the action both of dilute sulphuric acid and of muriatic (hydrochloric) acid. He also knew that when *nitric acid* was employed the “ air ” obtained was different and not inflammable. He therefore naturally concluded that the inflammable air came from the metal, and was, in fact, the mysterious *phlogiston* itself. The accepted explanation of combustion at that time was that phlogiston rushed out of the burning body into air deficient in phlogiston, and made it phlogisticated. Hence, when Priestley, in 1774, discovered a gas

(oxygen) which was especially favourable to combustion, he regarded it as having no phlogiston at all, and named it "dephlogisticated air." When Cavendish, in 1781, found that his *inflammable air* formed water when exploded with air, he still explained the reaction in terms of the phlogiston theory. It was the brilliant French chemist, Lavoisier, who first divined the full meaning of these discoveries, and named the *inflammable air* of Cavendish *hydrogen* (water-producer), and the *dephlogisticated air* of Priestley *oxygen* (acid-producer). He first correctly explained the phenomena of combustion, and showed that when carbon, sulphur, or phosphorus was burnt in oxygen the "acid" produced owed its origin to the union of the carbon, etc., with the oxygen. We now call these products of combustion acid-forming oxides (page 58), but Lavoisier called them acids.

Modes of preparation.—1. The student has already learned that hydrogen is evolved when hydrochloric acid or dilute sulphuric acid acts on any of the metals included in group B (page 74). The gas is very conveniently prepared by the action of dilute sulphuric acid on the metal zinc. Pieces of granulated zinc are placed in a Woulfe's bottle provided with a bent delivery-tube and a thistle funnel; sufficient water is then poured into the flask to cover the zinc, and on pouring strong sulphuric acid down the funnel, hydrogen is evolved with brisk effervescence, and may be collected over water (Fig. 5), after sufficient time has been allowed to elapse for the escape of the air contained in the apparatus.



Hydrogen so obtained is never pure; it may contain (1) hydrogen arsenide from the arsenic in

the zinc ; (2) oxides of nitrogen from the nitric acid in the sulphuric acid ; (3) sulphur dioxide and hydrogen sulphide if the sulphuric acid becomes heated during the reaction, because the nascent hydrogen then reduces the sulphuric acid ; (4) water vapour. These impurities can be removed by passing the gas through four U-tubes. The first is filled with broken

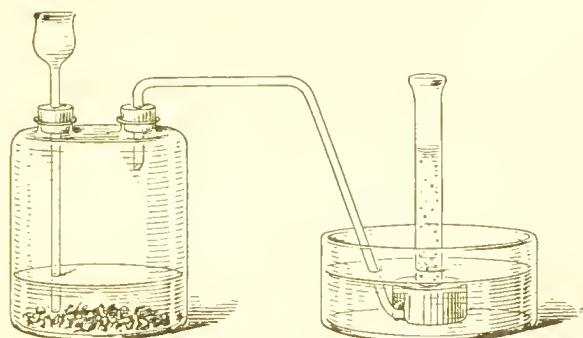


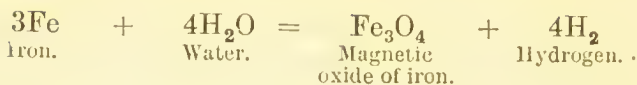
Fig. 5.—Preparation of hydrogen from zinc and dilute sulphuric acid.

glass moistened with lead nitrate solution: this removes the H_2S ; the second, with silver sulphate, which removes the AsH_3 ; the third contains caustic potash, which removes the SO_2 and oxides of nitrogen ; the fourth, strong sulphuric acid, which removes the water.

2. Hydrogen may be obtained from water :

(a) By the *electrolysis* of water (see page 103).

(b) By abstracting the oxygen from water, by passing steam over red-hot iron turnings contained in a heated iron pipe ; the iron unites with the oxygen of the steam to form the black magnetic oxide of iron (Fe_3O_4), and free hydrogen passes on. This constitutes Barff's process for coating articles made of iron with a thin coating of the magnetic oxide of iron, which forms an extremely hard surface, and effectually prevents any future rusting of the article.



(c) By the action of either of the metals potassium or sodium on water at ordinary temperatures. Both these metals are lighter than water, and if either of them be thrown upon water, a violent action takes place, hydrogen being evolved. If the hydrogen is to be collected, it is necessary to catch the piece

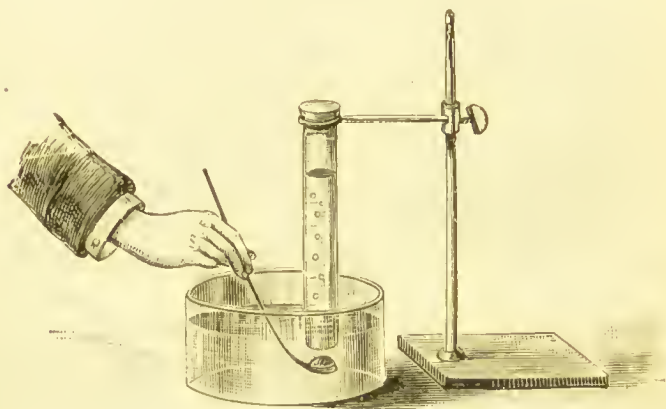


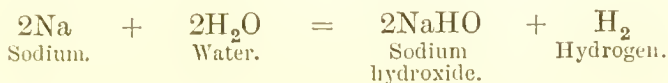
Fig. 6.—Preparation of hydrogen from potassium and water.

of potassium or sodium in some wire gauze, which is then held beneath the water under an inverted jar full of water, within which the hydrogen will then collect (Fig. 6).

A more convenient method is recommended in Newth's "Lecture Experiments." Small leaden sockets, easily made from common gas piping, are plugged with the sodium or potassium, which is then cut flush with the open end. A socket is placed on the floor of the trough beneath the mouth of the collecting jar.

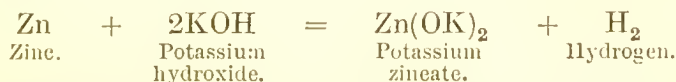
These metals liberate one-half of the hydrogen of

the water, uniting with the other half and with the oxygen to form the hydroxide of the metal, thus :



Barium, strontium, and calcium also decompose water at room temperature ; magnesium, aluminium, and iron decompose steam at about 100° , and other metals do so at higher temperatures.

3. Hydrogen may be obtained from *bases*, though not so easily as from acids. When granulated zinc is heated with a strong solution of caustic potash, hydrogen is evolved, thus :



Properties.—Hydrogen is a colourless, tasteless, and odourless gas. It was liquefied (1884) by Olszewski ; Dewar subsequently obtained it in larger quantity. He states that its specific gravity is 0.07 : it is therefore by far the lightest liquid known ; it is transparent and colourless, and boils at -253° , about 20° above the absolute zero (-273°) ; it solidifies at -257° to an ice-like solid of specific gravity 0.0763. It is the lightest gas known, and its specific gravity is represented as 1, the specific gravities of other gases representing the number of times they are heavier than hydrogen ; air is 14.4 times heavier than hydrogen. The weight of a litre of hydrogen, taken at 0° C. and 760 mm. barometric pressure, is 0.0896 grm., and is known as the *crith* (from *κριθή*, a barleycorn) ; 2 grm. of hydrogen at 0° C. and 760 mm. barometric pressure occupy 22.4 litres (this latter fact will be found extremely useful in

converting weights of various gases into volumes). Hydrogen is combustible, burning with an almost invisible flame if pure, and forming, by union with the oxygen of the air, water; it is a non-supporter of combustion.

By the term combustion, as ordinarily employed, is meant union with the oxygen of the air, such union being accompanied by the production of heat and light, so that combustion may be defined as oxidation in which the chemical action is sufficiently great to be accompanied by the evident production of heat and light. It must, however, be clearly understood that the terms *combustible* and *supporter of combustion* are purely relative. Thus, hydrogen is combustible in oxygen, and oxygen is a supporter of combustion; but if the atmosphere consisted of hydrogen, then oxygen would burn in it, and would be the combustible body, the hydrogen then being the supporter of combustion. Similarly, coal gas is a combustible substance, and is constantly seen burning in air, which then supports its combustion; the student, however, will presently learn (page 211) that air can also be made to burn in an atmosphere of coal gas.

The formation of water by the combustion of hydrogen can be demonstrated by allowing the jet of hydrogen to burn within a cool bell-jar, when the water condenses on the sides of the glass (Fig. 7).

The hydrogen flame is accompanied with the generation of intense heat, of which advantage is taken in the production of the lime-light. A jet of burning hydrogen (produced by the combustion of hydrogen with pure oxygen) is directed on to a piece of lime, the particles of which are raised to such a high temperature that they become incandescent, and, glowing at a white heat, emit the dazzling light known as the lime-light. The reason why the ordinary hydrogen flame emits no light is, that there is present

in it no solid matter that can be raised to a white heat and so emit light, for it is essential, for a flame to emit light, that there should be present in the flame some solid matter or dense vapour capable of being rendered incandescent. In the case of the lime-light, the lime is the solid matter that is introduced into the flame, and is rendered incan-

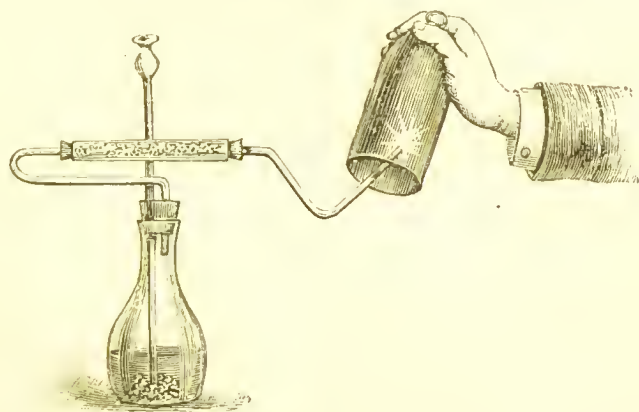


Fig. 7.—Formation of water by the combustion of hydrogen.

descent by the intense heat generated by the burning hydrogen.

When a light is applied to a mixture of hydrogen and oxygen, the union of the two gases is accompanied by an explosion; two *volumes* of hydrogen unite with one *volume* of oxygen, or two parts by *weight* of hydrogen with sixteen of oxygen, to form water.

Hydrogen is not appreciably soluble in water, nor is it, in the ordinary sense of the term, a poisonous gas, although it is incapable of supporting life. It is the most diffusible of all the gases. By *diffusion* is meant the property that all gases have of mixing with one another, even in opposition to the force of gravitation. Thus, if two flasks are taken (Fig. 8), the lower one filled with oxygen and the upper one

with hydrogen, and are connected by a long piece of narrow glass tubing passing through a perforated cork in each flask, although the heavier gas, oxygen, is at the bottom, and the lighter, hydrogen, at the



Fig. 8.—Apparatus for diffusion of gases.

top, yet the hydrogen will tend to diffuse downwards into the oxygen, and the oxygen will tend to diffuse upwards into the hydrogen, until the two gases are completely mixed. It is by this property of diffusion that a small quantity of a bad-smelling gas escaping,

say, into the corner of a room, soon demonstrates by its odour that it has become mixed with the entire atmosphere of the room.

All gases do not diffuse at the same rate: lighter gases diffuse more quickly than heavier ones; the relation existing between the rate of diffusion of a gas and its specific gravity is formulated in what is known as **Graham's law of the diffusion of gases**, which is, *that the rates at which gases diffuse vary inversely as the square roots of their specific gravities*. For instance, the specific gravity of hydrogen is 1, that of oxygen 16; the square root of the former is 1, of the latter 4; these numbers inverted give the rate of diffusion of hydrogen as four times that of oxygen.

Diffusion proceeds also through a porous partition, and these unequal rates may then lead, as in the kindred process of osmosis (page 39), to increased pressure on one side of the partition. The following experiment illustrates this: A Woulfe's bottle (Fig. 9, B) containing coloured water is well fitted with indiarubber corks, through which pass two glass tubes, c and d, open at both ends. The upper end of c passes through a well-fitting rubber cork into a porous pot A, containing only air. If A is surrounded by a glass jar, or beaker, filled with hydrogen from the apparatus H, the water will rapidly rise in the tube d. Hydrogen passes *into* the porous pot more quickly than air passes out, and the increased pressure thus produced causes the liquid to descend in c and to rise in d. If the glass jar is filled with carbonic anhydride or any other gas *heavier* than air, the liquid will move in the reverse direction, and be seen to rise in c. In this way, therefore, we can readily see whether a gas is lighter or heavier than atmospheric air.

Diffusion of liquids.—Graham also studied the

phenomena associated with the process of diffusion in the case of liquids, both when the two liquids were in direct contact with each other and when they were separated by a partition such as parchment or a vegetable or animal membrane. He

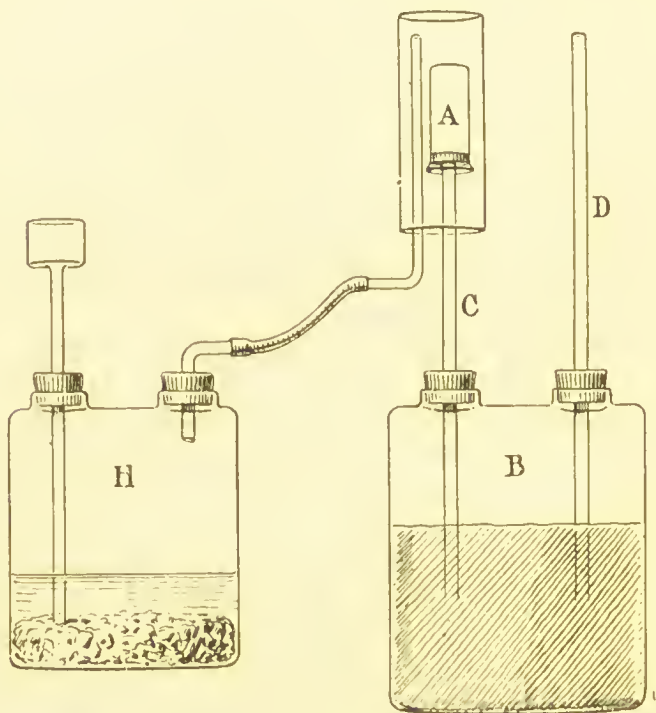
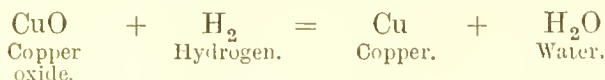


Fig. 9.—Experimental illustration of the diffusion of gases (see text).

thus recognised two principal classes of substances :
1. Those which in solution were able to pass through the membrane into the water beyond ; these he called crystalloids, as the class seemed to include crystalline substances—*e.g.* salt (sodium chloride).
2. Those which do not so pass through the membrane ; these he called “colloids” (κόλλα, glue), and they are, in fact, of a gelatinous nature more

or less resembling gum. The parchment and its supporting framework constitute a "dialyser," and the separation of colloids from crystalloids by its use is called "dialysis."

Hydrogen is a **reducing agent** (see page 76). For instance, if hydrogen be passed over fragments of red-hot copper oxide, the oxygen is abstracted by the hydrogen to form water, the copper oxide being *reduced* to the metallic state; thus:



Hydrogen in the "nascent" state—that is, at the moment of its release from combination—is specially effective as a reducing agent, and therefore frequently employed for the purpose.

In some respects hydrogen resembles the metals. It is liberated, like the metals, at the negative electrode. It is also absorbed by several metals, notably by palladium and platinum, forming metallic-looking alloys. To this *occluded* hydrogen, Graham gave the name *hydrogenium*. Liquid hydrogen, however, is unlike a metallic substance.

Test.—The best test for hydrogen is that it burns with an almost invisible flame, forming nothing but water. It is also, as we have seen, the lightest of all gases.

CHAPTER II

OXYGEN—OZONE

Oxygen: Modes of Preparation—Electrolysis—Ions—Properties—Oxygen and Respiration. Ozone: Preparation—Properties—Tests—Allotropy.

OXYGEN

Symbol, O ; molecule, O₂ ; atomic weight, 16 ; molecular weight, 32 ; liquefies at —183° ; freezes below —223° ; critical temperature —119°.

PROBABLY hexad, but seems only to exert the active valency of a dyad in ordinary circumstances. This valency is possibly increased to that of a tetrad at low temperatures.*

Oxygen is present to a very large extent in nature. In the compounds composing the solid crust of the earth it exists in considerable proportions, principally in chalk and limestone (calcium carbonate—CaCO₃), sand and flint (silica—SiO₂), and clay (aluminium silicate—Al₂Si₂O₇ + 2H₂O). It constitutes $\frac{8}{9}$ by weight of water, and about $\frac{2}{9}$ by weight of air. Its name is derived from *ὀξύς*, acid, and *γεννάω*, I produce (see page 90).

Modes of preparation.—1. By heating mercuric oxide (red oxide of mercury) :

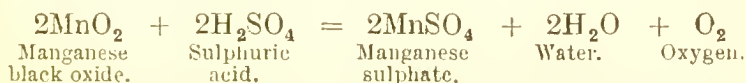


This method, although by no means the best one

* See Chemical Society's Annual Reports, 1904, p. 32.

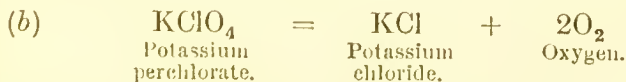
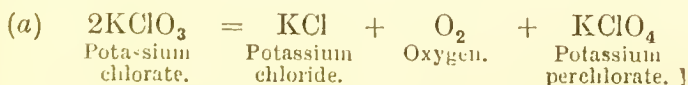
for obtaining oxygen, is of interest from the fact that it was in this way that oxygen was first obtained and discovered by Priestley on August 1st, 1774, when he heated the oxide with "a lens of twelve inches diameter and twenty inches focal distance." Mercury possesses the property, when heated to a temperature of 320° with exposure to air, of slowly absorbing oxygen from the air, and forming mercuric oxide, which, when the temperature is raised a little higher, evolves its oxygen, the metal mercury being left.

In 1775 oxygen was obtained independently by Scheele, by heating strong sulphuric acid with black oxide of manganese :



2. One of the best ways of obtaining oxygen, for experimental purposes, is by heating chlorate of potassium in a glass flask, to which is fitted a perforated cork and bent tube for conveying the gas to a pneumatic trough, where it can be collected over water (Fig. 10).

The whole of the oxygen of the chlorate of potassium is ultimately evolved, chloride of potassium being left; but the reaction appears to take place in two stages—



Potassium *perchlorate* is therefore less easily decomposed by heat than potassium *chlorate*.

3. Oxygen can be obtained from potassium chlorate at a much lower temperature by mixing

it with one-fifth of its weight of manganese dioxide. The chlorate when heated alone begins to evolve oxygen at about 370° ; but the mixture gives off its oxygen at 250° . The manganese dioxide is found unaltered at the end of the reaction, and can be used again with a fresh quantity of potassium

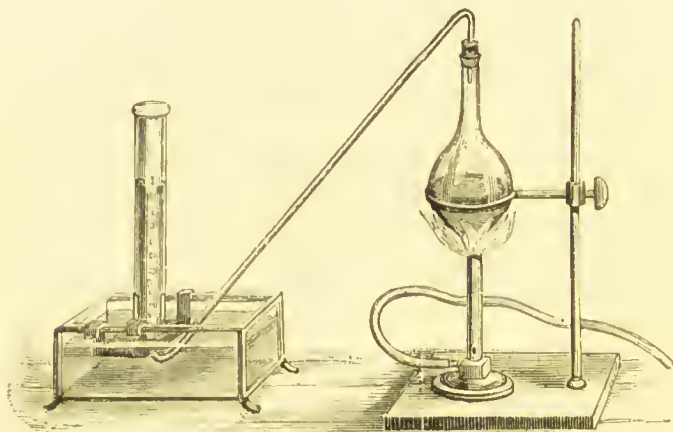
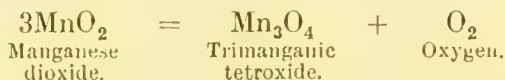


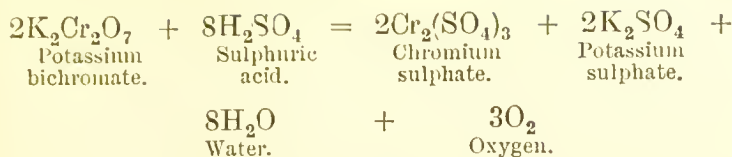
Fig. 10.—Preparation of oxygen.

chlorate. It is therefore a catalytic agent (page 77) in this reaction.

4. Oxygen may be obtained by strongly heating manganese dioxide (black oxide of manganese) in a gun-barrel closed at one end, and fitted at the other end with a perforated cork and tubing for carrying off the gas. The manganese dioxide only loses one-third of its oxygen, a lower oxide of manganese being left :



5. Oxygen may be obtained by heating powdered bichromate of potassium with strong sulphuric acid.



6. Oxygen may be obtained from water by two processes: (a) the electrolysis of water, and (b) decomposition of water by chlorine.

(a) *Electrolysis of Water*

This consists in the separation of the elements

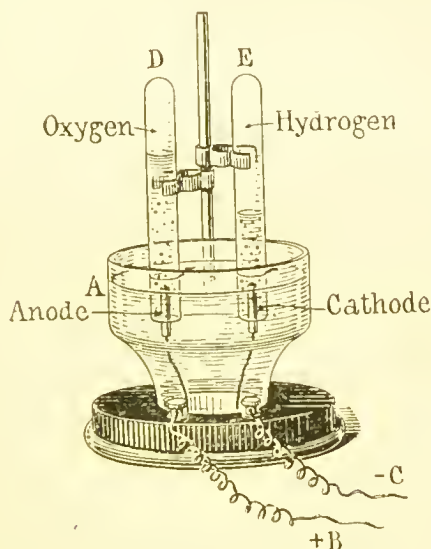


Fig. 11.—Electrolytic cell, or voltameter, as used in the electrolysis of water (see text).

of oxygen from water by means of a current of electricity. A glass vessel (Fig. 11, A) is taken, into which project two platinum electrodes, connected through the bottom of the vessel with the wires B and C, which in their turn are connected respectively with the positive and negative poles of a battery. Some water acidulated with sulphuric acid (to render it a better conductor of electricity) is placed in A,

and two glass tubes D and E are filled with this acidulated water, and then inverted over the platinum electrodes. When the circuit is complete, the "current of electricity" leaves the battery by the wire B, enters A at the positive electrode or **anode** (ἀνά, up, ὁδός, way), flows through the liquid to the negative electrode or **kathode** (κατά, down, ὁδός, way), whence it leaves A and returns to the battery by the wire C. During the passage of the current, bubbles of gas appear at the electrodes, whence they rapidly rise and collect in the respective tubes; the hydrogen collects in the tube E placed over the kathode, and the oxygen in the tube D over the anode. The volume of hydrogen evolved is double that of the oxygen, although if the volumes of the gases are very accurately compared, it will be found that the oxygen measures a little less than one-half the volume of the hydrogen, this slight difference being due to the greater solubility of oxygen in water, as compared with hydrogen.

Electrolytes.—When the conduction of electricity by a solution of a compound is accompanied by the separation of the constituents of the compound, as in the foregoing case, the compound is termed an electrolyte. Salts are usually good electrolytes. If a solution of copper sulphate (CuSO_4), for instance, be placed in the apparatus (Fig. 11) instead of acidulated water, we shall find no gas in E, but the kathode will become coated ("electroplated") with copper (Cu). Oxygen will collect in D, but this is due to a secondary chemical reaction: SO_4 , the negative constituent of the salt, is a compound radicle (page 26), and cannot continue in a free state; when separated at the anode it immediately reacts with the water present, combining with the hydrogen to form sulphuric acid (H_2SO_4) and liberating oxygen, which collects in

D. If an aqueous solution of potassium iodide (KI) be electrolysed, iodine (I) appears at the anode, but *hydrogen* collects in E, because the potassium (K), which really separates at the kathode, immediately decomposes the water (page 93).

Because oppositely electrified bodies attract, we call those elements or radicles which appear at the anode, or positive electrode, negative, and those which appear at the kathode positive. As already stated (page 17), metals are positive and non-metals negative.

Ions.—The phenomena associated with electrolysis were carefully examined by Faraday, who introduced the terms anode and kathode. He also called the separate constituents **ions** (ἰόν, one going); the one going to the anode, **anion**, and the one going to the kathode, **kation**. He showed, too, that the weight of an ion liberated at an electrode depends upon—

- (1) The strength of the current.
- (2) The duration of the current.
- (3) The equivalent (page 47) of the ion.

About 96,000 coulombs are required to liberate the equivalent.

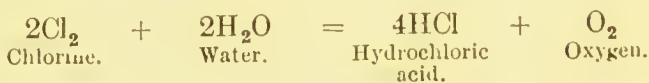
Faraday supposed that the current actually decomposed the salt into its constituent ions. We now believe that the salt in solution is always to a greater or lesser extent separated into its ions, or “ionised,” and that the current *directs* the anions to the anode and the kations to the kathode. As a certain proportion of ions, however, must be present in a given instance, the transference of some to the electrodes necessitates the automatic supply of fresh ones to fill their places; this is accomplished by the dissociation into ions of molecules hitherto not ionised. The current, although exerting only a

directive force, does in this way indirectly promote the gradual decomposition of the salt.

The student will naturally ask how potassium ion can be present in an aqueous solution of potassium iodide, and yet not decompose water as an atom of potassium does (page 93). The answer to this question is not yet certainly known. We must conclude that the ion differs from the atom in some respect, and that when transferred to the kathode it in some way gives rise to the atom, for at the kathode this action takes place. The whole question is one of great and growing importance, and no student can afford to neglect it. The commonest analytical reactions are effected by these energetic ions, not by the comparatively inert, undissociated molecules. The "**strength**" of a base or an acid depends on the proportion of ions in its solution. The solution of a strong base is rich in hydroxyl ions; the solution of a strong acid is rich in hydrogen ions.

(b) Decomposition of Water by Chlorine

If chlorine and steam be passed through a porcelain tube containing fragments of pumice-stone heated to bright redness, the chlorine unites with the hydrogen of the water, forming hydrochloric acid, and the oxygen is set free :

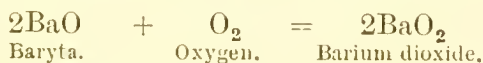


If the mixture of hydrochloric acid gas and oxygen be passed through a strong solution of caustic potash, the former is absorbed, potassium chloride being formed, and the oxygen is then obtained in the pure state.

7. Oxygen may be obtained from the atmosphere, in which it naturally occurs mixed with nitrogen

in the proportions of 21 volumes of oxygen to 79 of nitrogen. As there is no method of absorbing the nitrogen from a limited amount of air, and so leaving the oxygen in the pure state, the method that must be resorted to, if it is desired to obtain pure oxygen from the air, is to heat some substance in contact with the air, which at one temperature will absorb or combine with the oxygen of the air, and at another temperature will give up in a pure state the oxygen so taken from the air. The simplest process for effecting this is the baryta process. It is sometimes called the Brin process.

The baryta process.—This process depends upon the metal barium possessing two oxides, a lower one, baryta (BaO), and a higher one, barium dioxide (BaO_2). If baryta (BaO) be raised to a dull-red heat, and air be passed over it, the oxygen of the air is absorbed, converting the baryta into barium dioxide (BaO_2):



If now the barium dioxide be raised to a bright-red heat, it is resolved into baryta and oxygen, and so the oxygen absorbed from the air is obtained in a pure state:



Instead of decomposing the barium peroxide by raising the temperature, it has been found more advantageous to bring about the reaction by reducing the pressure in the tube or furnace containing the heated dioxide. Care is also taken to purify the air from carbon dioxide, etc., before passing it over the baryta. Thus modified, the process is now employed on a manufacturing scale for obtaining pure oxygen.

Properties.—The specific gravity of oxygen is 16; it is a little heavier than air. It is colourless, tasteless, and odourless. Although non-combustible, it is a powerful supporter of combustion, substances burning in oxygen much more brilliantly than they do in air. For instance, phosphorus burns with a most intense light in oxygen, and even a steel-wire spiral, tipped with a piece of burning tinder and

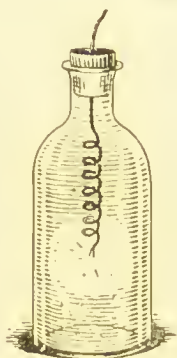


Fig. 12.—Combustion of steel spiral in oxygen.

placed in a jar of oxygen, will burn brilliantly, producing a shower of sparks (Fig. 12).

At -183° oxygen is converted into a pale blue liquid which is attracted by a powerful magnet, and is heavier than water; it has been solidified, and the solid has a specific gravity of 1.4256 at -252.5° .*

Oxygen is soluble in water, 100 volumes of water dissolving about 3 volumes of oxygen, and it is by means of this dissolved oxygen that fishes' blood, circulating through the gills, becomes aerated. Oxygen is, of course, non-poisonous, being the life-sustaining principle of the air; but if an animal be kept in pure oxygen it rapidly emaciates, on account of the increased waste of tissue substance

* Dewar, *Proc. Roy. Soc.*, 1904, lxxiii., 251.

due to the absorption of pure oxygen into the blood, and this occurs although the animal may be plentifully supplied with food, which it greedily devours.

Test.—The best test for pure oxygen is one depending upon its remarkable power of supporting combustion: if a piece of wood which has been made incandescent or glowing at one extremity be plunged into a jar of oxygen, it bursts into flame. A more delicate test is to add a little nitric oxide: this is a colourless gas which turns deep red when it comes into contact with free oxygen, being converted into nitric peroxide.

Oxygen in relation to respiration.—The oxygen of the air taken into the lungs, during inspiration, dissolves in part in the moisture covering the walls of the pulmonary air-cells, and so passes, by a process of osmosis, through the walls of the blood-capillaries into the blood, where it unites with the hæmoglobin, or colouring matter of the blood, to form a compound called oxyhæmoglobin. In this compound the oxygen is conveyed by the blood to all the tissues of the body, which abstract the oxygen from its loose union with the hæmoglobin, and undergo by means of it a process of combustion, and the heat resulting from these chemical changes suffices to maintain the temperature of the human body. One of the necessary and chief products of the oxidation of the animal tissues is carbon dioxide, which passes away in the expired air. There is thus a constant interchange of oxygen from the atmosphere, and of carbon dioxide from the blood, the air taken into the lungs losing four per cent. of oxygen and gaining in its place four per cent. of carbon dioxide. This carbon dioxide, which passes out in the expired air into the atmosphere, does not accumulate there, but is absorbed by the leaves of plants (through small

openings called *stomata*) and brought into contact with the chlorophyll or green colouring-matter of the leaves, which, during the day, decomposes the carbon dioxide into carbon and oxygen. The carbon is retained by the plant, and, uniting with the elements of water, becomes converted into sugar, starch, and other organic substances. The oxygen is returned to the air, and so the normal composition of the atmosphere is maintained.

Oxygen combines with every element, excepting fluorine, to form oxides.

Three classes of oxides are usually recognised:—

1. Acid-forming oxides, or anhydrides, already described (page 58).

2. Base-forming oxides, already described (page 58).

3. Peroxides. These seem to contain an extra atom of oxygen, which they lose on heating, either alone or with acids, and are then reduced to a lower, generally basic, oxide.

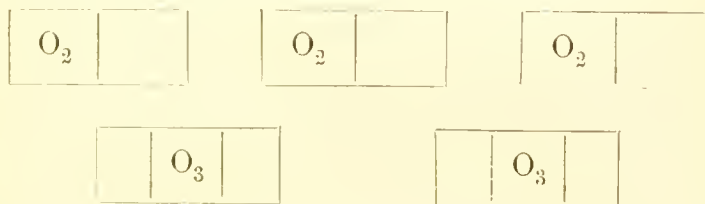
OZONE

Formula, O_3 ; molecular weight, 48.

Ozone (from ὄζω, I smell) is a peculiar form of oxygen. Its density is greater than that of ordinary oxygen, and its properties are different. Two volumes of ozone yield three volumes of common oxygen. It occurs naturally in the atmosphere in very small quantities, being produced from the oxygen of the air either by electrical currents generated during a thunderstorm, or by the weak currents of frictional electricity generated by the friction of large masses of water (such as the sea) against the air, or possibly by the evaporation of water and aromatic bodies (such as turpentine) in presence of sunlight.

Modes of preparation.—Ozone is prepared by effecting the condensation of three volumes of oxygen into two, but by whatever process this may be effected, it is impossible to convert all the oxygen into ozone. In other words, ozone cannot be obtained in a pure state, but always contains admixed oxygen, a mixture containing about 20 per cent. of ozone to 80 per cent. of oxygen being about the strongest that has ever been made. This condensation of oxygen into ozone may be effected in the following ways:—

1. By the silent passage of electricity through oxygen or air; the peculiar odour noticed when a frictional electrical machine is being worked is due to the production of ozone by this process. The change may be represented as follows, where the production of two ozone molecules from three oxygen molecules is depicted:—



or,

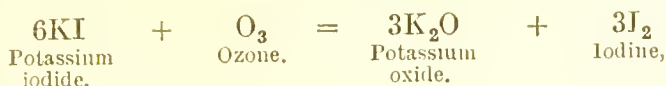


2. Ozone may be prepared by exposing a stick of phosphorus to moist and warm oxygen or air. This is best effected by placing a stick of phosphorus at the bottom of a bottle containing sufficient water to cover partially the phosphorus, loosely plugging the mouth of the bottle, and placing it for half an hour near a fire. At the end of that time ozone will be found in the air of the bottle, if the proper tests are applied.

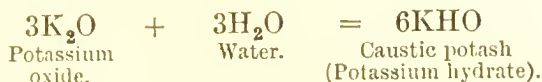
Properties.—The specific gravity of ozone is

24, and it is heavier than air; it is colourless, but possesses a peculiar odour which has been compared to that of diluted chlorine, or to phosphorus slowly oxidising. It is non-combustible, but is a supporter of combustion, and is slightly soluble in water. It is a powerful bleaching and oxidising agent, being capable of oxidising such metals as mercury and silver in the cold. It rapidly destroys cork, india-rubber, and other organic substances. It is an irritant to the eyes, nose, and bronchial tract, when present in the air in moderate quantities. It is completely converted to common oxygen when heated to 300° . Ozone is absorbed by turpentine, but oxygen is not.

Tests.—The ordinary method for detecting ozone in the air depends upon the power that ozone possesses of liberating iodine from iodide of potassium, the presence of free iodine being shown by the blue colour that it gives with a solution of starch. A piece of filter paper is moistened with a mixed solution of iodide of potassium and starch, and is then suspended for some time in a current of the air to be tested, when, if ozone be present, it will assume a blue colour. The objections to the validity of this test are that other bodies besides ozone may be present in the air, which also possess the property of liberating iodine from iodide of potassium, and so giving a blue colour to the starch; these bodies are chlorine and nitrogen tetroxide. It will be seen from the following equations that when ozone liberates the iodine from iodide of potassium it first forms potassium oxide, which, with water, forms caustic potash, a body that is alkaline to test-paper; whereas chlorine and nitrogen tetroxide, in liberating iodine from iodide of potassium, form respectively chloride of potassium and nitrite of potassium, both of which are neutral to test-paper.



then



So that the best test for ozone in the air will evidently depend, not on the liberation of iodine from iodide of potassium, since both chlorine and nitrogen tetroxide can effect this, but on ascertaining whether, with the liberation of the iodine, the solution of iodide of potassium becomes alkaline, for both chlorine and nitrogen tetroxide, in liberating the iodine from iodide of potassium, leave the solution neutral. The method of applying this modified and improved test for ozone in the air consists in exposing a solution of iodide of potassium coloured with red litmus to the air for some hours, in a shallow vessel, when, if ozone is present, the red colour changes to blue; whereas if chlorine or nitrogen tetroxide are present in the air, although they liberate the iodine from the iodide of potassium, yet the chloride of potassium and nitrite of potassium respectively formed, being neutral, are incapable of changing the colour of the red litmus.

That ozone consists of oxygen condensed in the ratio of three volumes to two can be shown by the following experiment:—

Some pure oxygen is enclosed in a graduated glass tube, furnished with platinum wires, standing over sulphuric acid, as this substance is not acted

on by ozone. Say 100 volumes of oxygen are taken, sparks are passed through the gas and the volume contracts, ozone being formed, to ninety-nine. These 99 volumes can now be brought into contact with turpentine which dissolves the ozone and leaves the oxygen. Suppose the volume is now ninety-seven. The total quantity of oxygen converted into ozone is therefore $100 - 97 = 3$ vols., and the ozone (as shown by the absorption with turpentine) is $99 - 97 = 2$ vols. In other words, three volumes of O_2 , when converted into O_3 , only occupy two volumes.

ALLOTROPY

When the same element is found in forms which possess different properties, the forms are described as **allotropic** (ἄλλος, another ; τροπος, condition). Ozone is an allotropic form of oxygen. The student will meet with other examples of allotropy in connection with carbon, phosphorus, and sulphur.

CHAPTER III

WATER—HYDROGEN DIOXIDE

Composition and Properties of Water—Water of Crystallisation—Natural Waters—Hard and Soft Waters—Mineral Waters—Hydrogen Dioxide.

WATER

Formula, H_2O ; molecular weight, 18:

Composition.—Water is composed of hydrogen and oxygen united in the proportion of two parts of hydrogen by weight to sixteen of oxygen, or, by volume, it is formed by the union of two volumes of hydrogen with one volume of oxygen. The composition of water may be proved in the following ways :

1. *The analytical method.*—By electrolysis (see page 103).

2. *The synthetical method.*—(a) By introducing a mixture of two parts by volume of hydrogen to one of oxygen into a eudiometer, and then exploding the mixture by means of an electric spark, when water will be formed. This may be effected in the Cavendish eudiometer (Fig. 13, A), which consists of a stout glass vessel, provided with a stop-cock at the lower part, and with two platinum wires fused through the glass at the upper part. The eudiometer is first exhausted of air by means of an air-pump, and is then filled with a mixture of two volumes of hydrogen to one volume of oxygen by connecting it with a bottle B containing the two gases in those proportions ; the stop-cock is closed and the eudiometer detached from B ; the gases may then be

exploded by means of an electric spark between the two platinum wires, the electricity being furnished by a charged Leyden jar c. By the explosion of the hydrogen and oxygen water will be formed, and will be deposited as a film upon the inner surface of the eudiometer, and the complete conversion of

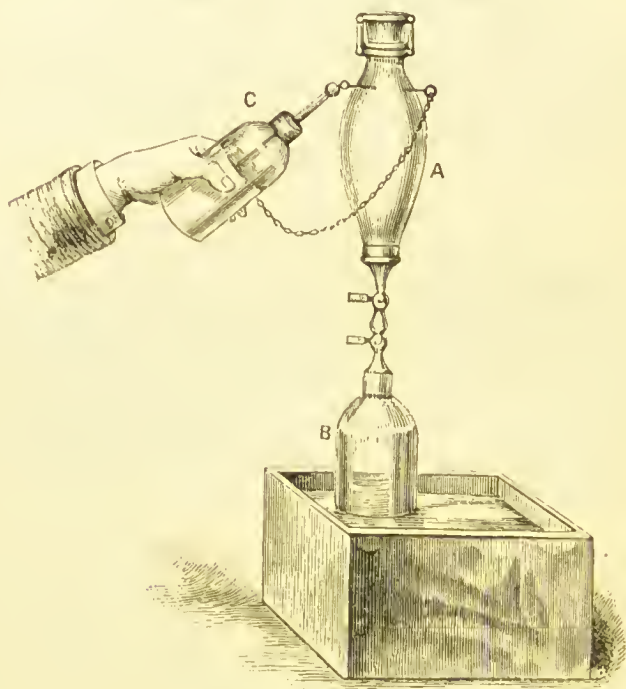


Fig. 13.—Formation of water by the explosion of hydrogen and oxygen in the Cavendish eudiometer.

these two gases into water will be demonstrated by the fact that, on opening the stop-cock of the eudiometer under water, the interior of it will be immediately and completely filled by the water, on account of the vacuum left within the eudiometer by the union of the hydrogen and oxygen, and the condensation of the resulting water as a film on the inner surface of the vessel.

A more instructive form of this experiment is that devised by Hofmann (Fig. 14). A U-shaped tube A, closed at one end and open at the other, is partly filled with a mixture of two volumes of hydrogen and one volume of oxygen, the gases being enclosed by mercury in the bend of the tube. The closed limb A of the U-tube is furnished with two platinum wires at its upper end and is graduated. It is surrounded by a second tube B, through which passes a stream of vapour from the boiling amylie alcohol in the flask. By this means the tube A is kept at a temperature of 130° , well above the boiling-point of water. As soon as the expansion produced by the heating of the gases by the boiling alcohol vapour has ceased, the open end of the tube is temporarily closed by a cork, and the gases are exploded by passing a spark between the platinum wires. On removing the cork and levelling the mercury, it will be seen that the three volumes of H and O have condensed to two volumes of steam, and if the stream of hot vapour be stopped, these two volumes of steam will condense to a minute drop of water, and the mercury will rise to the top of the tube.

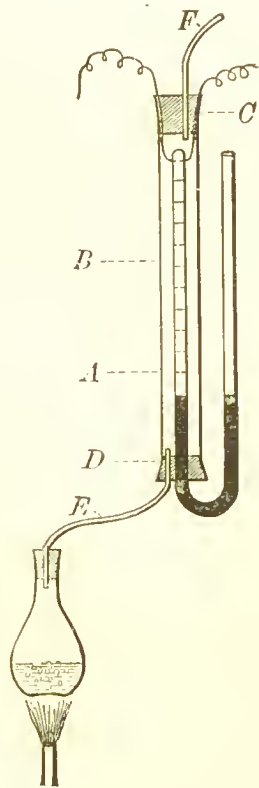


Fig. 14.—Hofmann's experiment.

(b) The composition of water by weight was proved by Dumas in 1843 by passing pure dry hydrogen over a known weight of oxide of copper contained in a bulb, and heated to redness. The

hydrogen unites with the oxygen of the oxide of copper to form water, and so reduces the oxide to the condition of metallic copper.



The water, which passes away from the tube in the form of steam, may be collected in a previously-weighed ehloride of caleium tube, the increase in weight of which at the end of the experiment will give the amount of water produceed, while the loss of weight of the copper oxide will give the weight of oxygen.

Properties.—Pure water in thin layers is a colourless liquid, but if viewed through a tube six feet in length which is filled with it, and which is blackened at the sides and provided with glass ends, it is seen to possess a faint blue colour—a colour that is also well seen in glaeier ice, in deep sea-water, and in the Croydon swimming bath, where the water from deep chalk wells is used. The presenee of a very small amount of animal organic matter (sewage), or of vegetable organic matter (peat), will eause the blue colour of the water to be replaeed by a yellow or brownish tint. Pure water is tasteless and odourless; its specific gravity is 1, that is, it is chosen as the standard with which the weights of equal volumes of all other liquids and solids are compared; it freezes at 0° C., and boils at 100° C., under the normal atmospheric pressure. A large number of solids and gases are **soluble** in water. Some liquids, such as alcohol and glycerin, are **miscible** with water in all proportions; others, such as ehloroform and ether, only in small proportions; and others, such as olive oil and eastor oil, not at all. Many solid chemical substances are capable of forming a loose chemical union with water, which

in this solid form is then known as **water of crystallisation**. *Examples:* Sodium carbonate ($\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$), zinc sulphate ($\text{ZnSO}_4, 7\text{H}_2\text{O}$), copper sulphate ($\text{CuSO}_4, 5\text{H}_2\text{O}$).

Water of crystallisation is capable of being expelled or driven off by heat, but there are some crystalline bodies that slowly part with their water of crystallisation by simple exposure to the air. This phenomenon of the spontaneous loss of water of crystallisation on exposure to the air is known as **efflorescence**, and such bodies are called **efflorescent** (from *efflorescens*, blossoming forth), on account of their assuming a powdery condition; for instance, ordinary washing soda ($\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$) is a good example of an efflorescent body, crystals of it, on exposure to dry air, losing their water of crystallisation, and becoming opaque and powdery. On the other hand, **deliquescence** is the power possessed by certain solid substances of absorbing moisture from the air to such an extent as to become moist and finally liquid, from the solid dissolving in the absorbed water; such bodies are called **deliquescent** (from *deliquescens*, melting away), on account of the liquefaction which they undergo on exposure to the air. Calcium chloride and potassium carbonate are two good examples of deliquescent substances, as they soon become liquid on exposure to the air.

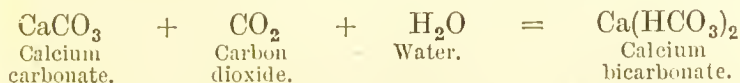
Sources and varieties of water as used for drinking purposes.—Rain and snow are the natural sources from which drinking waters are derived. Rain, when it falls upon the surface of the earth, is disposed of in three ways: (1) part of it is returned to the atmosphere by evaporation; (2) part of it flows according to the inclination of the surfaces, and so contributes to the formation of brooks, streams, and rivers; (3) part of it sinks or percolates into the

soil until it reaches an impermeable stratum of hard rock or clay, and so forms the underground sources of water that are made available for the use of man either by coming to the surface as springs or by being tapped by the sinking of wells or by pumps.

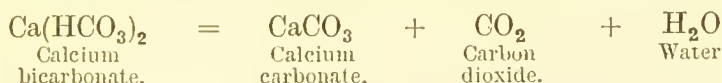
Rain-water as it leaves the clouds is pure, but in its passage through the air it may absorb and collect many substances, such as oxygen, carbon dioxide, traces of ammonia, sulphur dioxide, nitrogen tetroxide, chlorine, sodium chloride (if in the vicinity of the sea), particles of soot, and various fungoid and bacterial organisms. The rain-water percolating through, or flowing over, the soil may dissolve from it various substances, such as lime salts, magnesia salts, etc. Rain-water is a very soft water, and is therefore useful for washing purposes. A **soft water** is one in which soap can dissolve, and therefore readily form a lather without being precipitated; a **hard water**, on the other hand, is one in which soap, as fast as it dissolves, is precipitated by some substance or substances present in the water, and so the formation of a lather is rendered difficult. The hardness of a water is caused by the presence of calcium and magnesium salts, and may be temporary or permanent, or a combination of the two.

Temporary hardness is that which can be removed by boiling, and is due to the presence of the soluble bicarbonates of calcium and magnesium, which on boiling are converted into the insoluble carbonates of those metals, and these, being deposited, constitute the *fur* that accumulates in kettles and boilers. Temporary hardness is acquired by rain or stream water, containing carbon dioxide in solution, flowing over some form of calcium carbonate (chalk or limestone), or magnesium carbonate in the soil; such water containing carbon dioxide

in solution is capable of forming a soluble bicarbonate with either of these carbonates, thus :

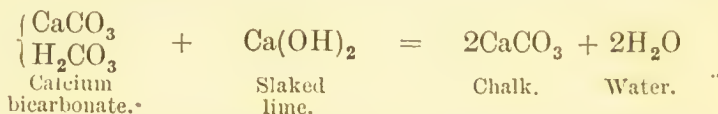


This soluble bicarbonate loses part of its carbon dioxide on boiling, and the insoluble calcium carbonate is once more formed and deposited, thus :



Permanent hardness is that which cannot be removed by boiling, and is generally due to the presence of calcium or magnesium sulphate. In the case of sea-water the hardness is due to sodium chloride, which renders ordinary soap insoluble (*see* page 507). The difficulty experienced with a hard water of obtaining a lather with ordinary soap (which consists mainly of sodium oleate and stearate) is thus explained : as soon as some of the soap dissolves, it is converted into the insoluble calcium or magnesium oleate and stearate, and not until all the calcium salts are thus precipitated do we get a solution of soap which forms the lather. The use of hard water, therefore, entails great waste of soap. To prevent this the water must be softened, which may be effected, if the water is only to be used for washing purposes, by adding a little sodium carbonate, when all the calcium and magnesium salts will be precipitated as carbonates, and after allowing these to subside the clear water will be quite soft. Another process, which is applicable to drinking water, and is known as Clark's process, consists in adding a weighed quantity of slaked lime to a known bulk of the water, when the whole of the lime added and the lime to which the temporary hardness is

due is precipitated. The reaction is represented by the equation :



It will be noticed that one molecule of calcium hydrate is required to precipitate one molecule of the bicarbonate.

The best method of purifying water is by distillation; when all the solid impurities are left behind in the still. The first and last portions of the distillate should be rejected.

The principal constituents of three typical river waters are given below—the Dee, in Wales, which, flowing over hard insoluble rocks, slates, etc., is a typical soft water; the Thames, which cuts through the chalk and has much temporary hardness; and the Trent, which contains much calcium sulphate and sodium chloride.

	THAMES.	TRENT.	DEE.	
Calcium carbonate..	10·8	0·32	0·85	grs. per gal.
Calcium sulphate ..	3·0	21·55	0·12	„
Salt ..	1·8	17·63	0·72	„
Organic matter ..	2·36	3·68	1·54	„

Sea-water contains 3 to 4 per cent. of salts, chiefly sodium chloride (1,850 grains per gallon) and magnesium salts.

Drinking water is purified by filtration through beds of sand and gravel, during which process much of the organic matter is oxidised, probably by the combined action of bacteria and the oxygen of the air.

Mineral waters.—These are spring waters containing in solution some medicinal ingredient. In the following table the more important mineral

waters are enumerated, with their sources and composition :

SOURCE	COMPOSITION
Vichy Carlsbad Ems Selters Malvern Apollinaris	} Alkaline waters, containing sodium carbonate and bicarbonate; effervescence due to carbon dioxide.
Spa	
Tunbridge	
Some Cheltenham waters	
Harrogate	
Aix-la-Chapelle	
Leamington Epsom	} Aperient saline waters, containing magnesium sulphate.
Cheltenham Scarborough	
Bath Bristol Matlock	} Calcareous waters, containing calcium bicarbonate and calcium sulphate.

Solvent action of water.—Many substances are soluble in water. As a rule, boiling water dissolves a larger quantity of a solid substance than cold water. When water has dissolved the maximum quantity of a substance, the solution is said to be "saturated." If a saturated solution be made at the boiling-point and the solution be allowed to cool, the excess dissolved at the boiling-point over the quantity dissolved at the ordinary temperature separates out, usually in crystals. This process is

largely used in purifying substances by "recrystallisation." One notable exception to the above rule is common salt, which dissolves almost as readily in cold as in hot water. Some of the calcium compounds ($\text{Ca}(\text{HO})_2$ and CaSO_4) are slightly more soluble in cold than in hot water.

The solubility of *gases* in water depends (1) upon the nature of the gas: thus 1,000 vols. of ammonia dissolve in 1 vol. of water, while only .02 vol. of hydrogen dissolves in 1 vol. of water; (2) on the temperature: the lower the temperature of the water the greater is the volume of the gas dissolved; by boiling the water the dissolved gases are therefore expelled; (3) on the pressure: the same *volume* is dissolved at all pressures, if measured at the pressure at which it is dissolved; but since by Boyle's law (page 32) the same *volume* contains different *weights* of gas proportional to the different pressures, it follows that the *weight* of gas dissolved in any volume of water will be directly proportional to the pressure. In this form the statement is known as the **Law of Henry and Dalton.**

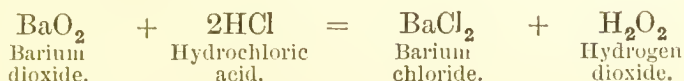
HYDROGEN DIOXIDE

Formula, H_2O_2 ; molecular weight, 34.

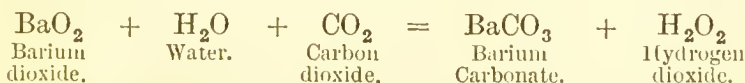
Water and hydrogen dioxide constitute the two oxides of hydrogen. Hydrogen dioxide is also known as peroxide of hydrogen, and as oxygenated water, the latter name being given to it on account of the facility with which it decomposes into water and oxygen.

Modes of preparation.—1. Hydrogen dioxide may be obtained by the action of any dilute acid on barium dioxide. Thus, if diluted hydrochloric acid be added to barium dioxide, double decom-

position takes place, barium chloride and hydrogen dioxide being formed :



Hydrochloric acid, however, is not a convenient acid to use in the preparation of hydrogen dioxide, since this latter body is contaminated by the presence of the soluble barium chloride. It is therefore preferable to select an acid which will yield an insoluble barium salt, and so leave only the hydrogen dioxide in solution ; carbonic acid answers these requirements admirably. If carbon dioxide be passed through water containing barium dioxide suspended in it, carbonate of barium is precipitated and a pure solution of hydrogen dioxide obtained.



2. Hydrogen dioxide is said to be obtained as one of the products of the atmospheric oxidation of several of the natural volatile oils in presence of moisture, such as the oils of turpentine, pine, eucalyptus, etc.

Properties.—Hydrogen dioxide is a syrupy liquid, but is usually sold mixed with water of such a strength that 1 volume, when treated with an acid solution of potassium permanganate, evolves about 20 volumes of oxygen. It is colourless and odourless, but possesses an astringent taste, and is miscible with water in all proportions. It resembles peroxides in general (page 110), and readily gives up its extra atom of oxygen :



This decomposition may be brought about by boiling, or by bringing it in contact with bodies in want of oxygen, when the hydrogen dioxide readily parts with one-half of its oxygen; it is in this way that it acts as a disinfectant and deodoriser. Hydrogen dioxide is also a powerful bleaching agent by virtue of its power of rapidly oxidising colouring matters; its effect as a so-called hair-dye, in turning the hair yellow or white is simply that of a bleaching agent.

Test.—As we should expect, hydrogen dioxide acts like an oxidising agent and liberates iodine from iodide of potassium, the liberated iodine turning starch solution blue; this is a property, however, possessed by other substances, but unlike all these other oxidising agents (page 76), hydrogen dioxide will liberate the iodine from iodide of potassium in presence of ferrous sulphate.

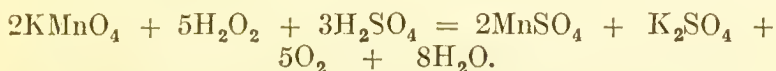


The caustic potash produced is neutralised by the dilute acid present in ordinary solutions of the peroxide.

If hydrogen dioxide be poured on some black oxide of manganese, an effervescence takes place, owing to the escape of oxygen. This enables us to test the strength of a solution of peroxide of hydrogen by measuring the volume of oxygen evolved. When peroxide of hydrogen is mixed with chromic acid and a little ether, the ether is coloured a beautiful blue, owing probably to the formation of perchromic acid, HCrO_4 .

It is important, however, to remember that hydrogen dioxide can also act as a reducing agent (page 76), and discharge the colour of an aqueous solution of potassium permanganate acidulated with sulphuric acid. Half of the oxygen evolved

in the reaction comes from the dioxide and half from the permanganate.



The reaction provides a convenient method for estimating the amount of H_2O_2 present in a suitable solution (*see* page 599); 1 c.c. standard $\text{KMnO}_4 = .0017$ gm. of H_2O_2 .

CHAPTER IV

NITROGEN—THE ATMOSPHERE

Nitrogen: Modes of Preparation, etc.—The Atmosphere:
The Argon Group of Gases—Principal Constituents
of the Atmosphere — Minor Constituents — Other
Substances.

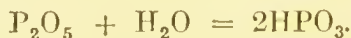
NITROGEN

Symbol, N ; molecule, N₂ ; pentad ; atomic weight, 14 ; molecular weight, 28 ; liquefies at —194° ; freezes at —214° ; critical temperature, —149°.

NITROGEN (meaning *generator of nitre*) owes its name to the fact that it is an essential constituent of nitre (nitrate of potash). Nitrogen is widely and extensively distributed in nature ; it constitutes four-fifths of the atmosphere by volume ; it is present in all natural nitrates, and forms an important constituent of the tissues and organs of all animals and plants ; in animals it is present in albumin, fibrine, cartilage, casein, urea, etc. ; in plants it is present in vegetable albumin and in all alkaloids.

Modes of preparation.—1. Nitrogen may be obtained by removing the oxygen from a limited volume of air by any of the following processes :—

(a) By burning phosphorus under a bell-jar standing over water ; the phosphorus consumes all the oxygen of the air contained in the bell-jar, forming a white powder—phosphorus pentoxide (P₂O₅)—which dissolves in the water, forming metaphosphoric acid (HPO₃) :



If the aqueous solution of metaphosphoric acid is

heated for some time, orthophosphoric acid is formed :



After the combustion is completed the water rises in the jar to a higher level than at first. The gas within the bell-jar now occupies four-fifths of the original volume of the air taken, and consists of nitrogen.

(b) By absorbing oxygen from a confined volume of air by means of a solution of pyrogallate of potassium.

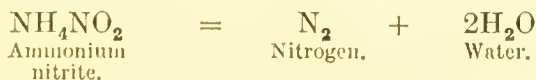
(c) By passing air over red-hot copper turnings contained in a long porcelain tube, when the copper unites with the oxygen of the air to form copper oxide (CuO), and pure nitrogen passes on. This reaction is much facilitated by adding a little ammonia (NH_3) to the air.

(d) By exploding in a eudiometer 42 volumes of hydrogen with 100 volumes of air (the latter containing just 21 volumes of oxygen), when the hydrogen and oxygen will unite to form water, which will condense on the sides of the eudiometer, and nitrogen will remain.

2. Nitrogen may be very readily obtained by boiling together solutions of potassium nitrite and ammonium chloride, when double decomposition between the two salts first takes place, resulting in the formation of ammonium nitrite and potassium chloride.



The ammonium nitrite then splits up into nitrogen and water.



3. Nitrogen may also be prepared by passing chlorine into solution of ammonia, when ammonium chloride is formed and nitrogen evolved.



In this process care must be taken to keep the ammonia in excess, otherwise the chlorine would act upon the ammonium chloride, forming the terribly explosive chloride of nitrogen.

Properties.—The specific gravity of nitrogen is 14, and it is a little lighter than air. The properties of nitrogen are mainly negative; it is odourless, tasteless, colourless, not combustible, a non-supporter of combustion, and but slightly soluble in water; it is not poisonous, since the air contains about four-fifths of it by volume, but it is incapable of supporting life by itself. The main function of the nitrogen of the atmosphere is to dilute down the oxygen, which would otherwise be too energetic in its action.

Test.—A lighted taper, if plunged into a jar of nitrogen, is immediately extinguished, and the gas itself does not ignite. The only other odourless, or comparatively odourless, gas that behaves in this way is carbon dioxide, and the two may be readily distinguished by carbon dioxide turning lime-water milky, whereas nitrogen has no effect upon lime-water. So that the combined facts of an odourless gas extinguishing a lighted taper, being non-combustible, and not turning lime-water turbid, will indicate that the gas is nitrogen.

THE ATMOSPHERE

Specific gravity = 14.4 (H = 1).

The atmosphere mainly consists of a mixture of oxygen and nitrogen in the following proportions:—

			By volume.		By weight.
Oxygen	21	..	23
Nitrogen	79	..	77

In 1785 Cavendish, in the course of his classical "Experiments on Air,"* had noticed that when the nitrogen of the air combined with oxygen there remained a gas which would not so combine, and he even estimated the amount of this inert gas as not more than $\frac{1}{120}$ of the nitrogen; the fraction is now stated† to be $\frac{1}{84}$. Anyone acquainted with the extreme thoroughness and accuracy of Cavendish's experimental work may be forgiven for suspecting from this discrepancy that possibly the fraction may really, in the course of the century, have slightly increased.

By 1893 Lord Rayleigh had established the fact that the "nitrogen" of the atmosphere was for some reason or other heavier than chemical nitrogen—e.g. nitrogen obtained from ammonia. This increased density was completely explained when, in 1894, Lord Rayleigh and Professor Ramsay announced their discovery of a new element in the atmosphere, which they subsequently named **argon** (*ἀργόν*, not working, idle), and found to have a density 20 ($H = 1$). The molecular weight of argon will therefore be 40, and, since the molecule is believed to be monatomic, the atomic weight will also be 40. In 1898 Sir William Ramsay, who had meanwhile discovered **helium**, proved that the supposed element argon was really a mixture of true argon with minute quantities of other gases; these he further identified after close and protracted investigation, and named **neon**, **krypton**, and **xenon**. He states‡ that they are present in the

* Reprinted as No. 3 of the Alembic Club Reprints.

† By Sir Wm. Ramsay, in "Gases of the Atmosphere," p. 144.

‡ "Gases of the Atmosphere," p. 257.

atmosphere, approximately, in the following proportions by volume :

Helium	1 part in 245,300*		Argon	1 part in 106·8
Neon	1 „ 80,800*		Krypton	1 „ 20 millions
Xenon			1 part in 170 millions.	

All appear to be chemically inert, with monatomic molecules, and find places in the same column in the periodic table (page 88).

Gases emanating from radioactive substances are also believed to be present in the atmosphere.

Other bodies are, or may be, present in the air in small quantities. In the following list are enumerated all the constituents of the atmosphere, divided into three groups: 1, the principal constituents; 2, minor constituents, believed to be *always* present though in small quantities; and 3, occasional constituents of the atmosphere.

Oxygen	}	Principal constituents of the atmosphere.
Nitrogen		
Water (in the form of aqueous vapour, clouds, or mists)	}	Minor constituents of the atmosphere probably always present.
Carbon dioxide		
Helium, neon, argon, krypton, xenon, radioactive gases		
Ammonia		
Nitrous and nitric acids		
Hydrogen peroxide		
Hydrogen		
Ozone	}	Constituents that are sometimes present in the atmosphere in small quantities.
Sulphur dioxide and sulphurous and sulphuric acids		
Chlorine		
Sulphuretted hydrogen		
Carbonic oxide		
Particles of soot		
Fungoid and bacterial organisms		

* Later estimates, by H. E. Watson, give helium 1 in 185,000, and neon 1 in 55,000 (*Proc. Chem. Soc.*, 1910, p. 82.)

As previously stated, oxygen and nitrogen so nearly make up the entire bulk of the atmosphere that, in indicating the percentage composition of the air, it is customary to make the percentages of these two gases add up to 100, although actually a small fraction of the percentage composition should be reserved for the other constituents of the air.

In describing the chemistry of the atmosphere, it will be convenient to discuss separately the constituents of the air, in the order above given in the three divisions.

1. THE PRINCIPAL CONSTITUENTS OF THE ATMOSPHERE—OXYGEN AND NITROGEN

Methods of determining the composition of the atmosphere.—(1) *The eudiometric method.*

—By this method the amount of oxygen in the air is determined by observing the contraction that takes place after exploding a known volume of air in a eudiometer with excess of hydrogen; since two volumes of hydrogen unite with one volume of oxygen to form water, one-third of the contraction will be due to oxygen, and so the proportion of oxygen present in the known volume of air will be ascertained.

(2) *Estimation of oxygen and carbon dioxide in air, or other gaseous mixtures, by absorption.*—Oxygen is readily absorbed by an alkaline solution of potassium pyrogallate, and the volume of the gas present in a measured volume of air may therefore be determined as follows:—

A Hempel absorption pipette (P), Fig. 15, is filled to the level indicated by the dotted line with a solution freshly prepared by mixing one measure of aqueous solution of pyrogallie acid (25 per cent.) with six measures of aqueous solution of caustic potash (60 per cent.).

The Hempel burette, represented in Fig. 16, consists of a plain pressure tube A, connected at the foot by thick rubber tubing with a graduated tube B, which is fitted with a tap T. To use the apparatus, A and B are placed side by side on the table, T is opened, and water is poured into A till it rises to a convenient level in B; it will also be at the same horizontal level in A. On raising A the water will rise in B, and should be able to rise to T without quite emptying A. The amount of water having been thus adjusted, A and B are replaced side

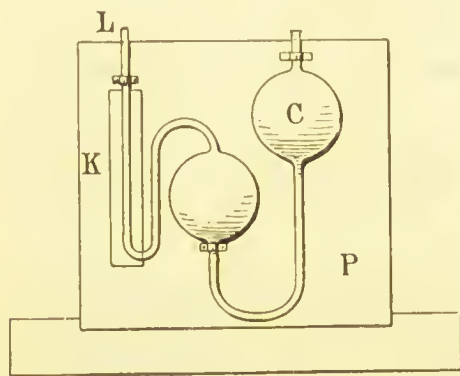


Fig. 15.—The Hempel pipette, P, with capillary branch, K.

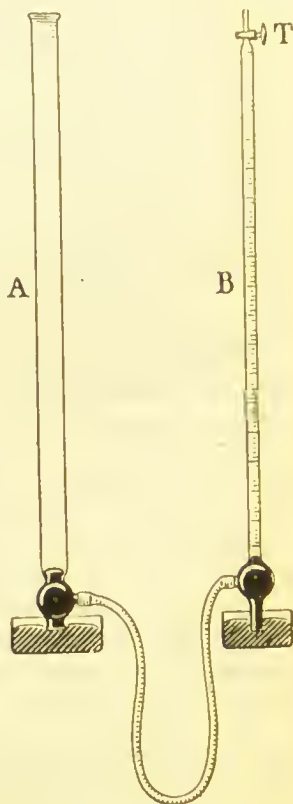


Fig. 16.—The Hempel burette.

A, Pressure tube.
B, Measuring tube.
T, Tap.

by side, and the water allowed to return to the same horizontal level in both. T is now turned to close B, which now contains a measured volume of air at atmospheric pressure and at room temperature. This volume must be read and recorded.

The nozzle of B is now connected, by a short piece of thick rubber tubing, with the end L of P, which is placed very near for the purpose. T is now opened, and the level of the liquid observed in the capillary branch K, which rests against a white background. It should remain at rest. On now raising A the air in B will be forced into P and will drive back the solution, which will be seen to rise in C. On presently lowering A, the solution will descend from C and return to K. When it reaches the original level, T is again turned to close B. The position of A is now adjusted till the water stands at the same horizontal level in A and B. The volume of air in B is then again read and recorded. It will be found to be less than the original volume. The difference is the volume of oxygen absorbed by the solution. T is again opened, and the whole process repeated. When no further diminution takes place, the experiment is complete.

It is clear that any other constituent in the air which is absorbed by this solution will also be counted as oxygen. Carbon dioxide is absorbed by caustic potash and will be absorbed by the solution, which contains free potash. In ordinary air, however, there is usually so little carbon dioxide that the error would not be appreciable with this apparatus. If we have any doubt of this in a particular case, we should first absorb the carbon dioxide from our sample of air by connecting it with a similar pipette to P containing a solution of caustic potash (20 per cent.) instead of the pyrogallate. Proceeding exactly as before, we can remove the carbon dioxide and estimate its volume, if appreciable. We can then change the pipette for P and estimate the oxygen as described.

(3) *The copper method.*—In this process a previously-weighed tube containing copper turnings is

raised to a red heat, and a known weight of air is then passed through it; the copper unites with the oxygen of the air, forming oxide of copper, and the nitrogen may be allowed to pass on into a glass globe provided with a stop-cock, which has been previously exhausted of air at the air-pump and then weighed; at the end of the experiment the increase in weight of the tube containing the copper turnings will give the amount of oxygen contained in the weighed quantity of air experimented with, while the increase in weight of the previously exhausted globe will give the amount of nitrogen.

(4) *The synthetical method.*—This consists in mixing together oxygen and nitrogen in the proportion of 21 volumes of oxygen to 79 volumes of nitrogen, when a mixture possessing all the properties of air will be obtained.

The atmosphere a mixture of oxygen and nitrogen, not a compound of those gases.—

That the atmosphere is simply a mechanical mixture of oxygen and nitrogen, and not a chemical compound of those two gases, may be proved in various ways.

(1) *By the method of mixture.*—This consists, as just described, in mixing together 21 volumes of oxygen with 79 volumes of nitrogen, when no heat is evolved or absorbed; neither is there any change of volume or colour; in fact, there is no sign of any chemical action, and yet the resulting mixture possesses all the physical and chemical properties of air.

(2) *By solution in water.*—Dissolved air is different in composition from ordinary air. If the air were a chemical compound of oxygen and nitrogen, then mere solution in water would be unable to alter its composition, whereas if it be a mixture of the two gases, then, on account of the greater solubility of

oxygen in water as compared with nitrogen, the dissolved air should be richer in oxygen than ordinary air; this is actually the case.

If air be well agitated with water, and then the dissolved gas expelled by boiling the water and collected in a tube, it will be found, on making an analysis of this dissolved gas, that it contains more oxygen than ordinary air, as shown in the following table :—

			Composition by volume of			
			Ordinary air.		Dissolved air.	
Oxygen	21	..	35
Nitrogen		79	..	65

(3) *By the diffusion experiment.*—If the air were a chemical compound of oxygen and nitrogen, then on submitting it to the process of diffusion it would

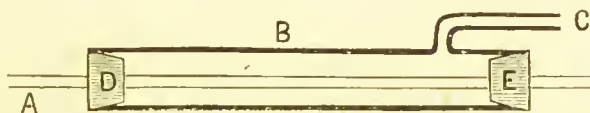


Fig. 17.—Diffusion apparatus for proving air to be a mixture of oxygen and nitrogen.

diffuse unchanged in composition, since by diffusion alone it is impossible to separate the constituents of gaseous chemical compounds; but if it be a mechanical mixture of oxygen and nitrogen, then on submitting it to diffusion the relatively lighter gas nitrogen should diffuse at a greater rate than the heavier oxygen (*see* Graham's "Law of Diffusion," page 97), and this is actually what does take place.

Fig. 17 represents the diffusion apparatus for proving that the atmosphere is a mechanical mixture of oxygen and nitrogen.

A is a porous tube, consisting of unglazed porcelain, passing through two perforated india-rubber corks D and E; B is a stout glass tube fitting tightly

over the corks D and E, and provided with an arm or outlet, C, by which it can be connected with an air-pump. By this means it is possible to produce a vacuum in B, and around that portion of the porous tube A lying between the corks D and E; if, now, air be passed through A it will tend to diffuse through the porous tube into the vacuum in B, and on examining this air which has diffused through into B it will be found to be richer in nitrogen than ordinary air, owing to the lighter nitrogen having diffused through the pores of the tube A at a greater rate than the heavier oxygen. This separation by diffusion could only take place from a mechanical mixture of the two gases, and not from a chemical compound.

(4) The relative weights of nitrogen and oxygen in the air are not simple multiples of their atomic weights 14 and 16.

(5) The composition of the air is not quite constant.

2. MINOR CONSTITUENTS OF THE ATMOSPHERE PROBABLY ALWAYS PRESENT

(1) **Aqueous vapour.**—This is derived by evaporation from large masses of water, such as the sea, lakes, rivers, etc.; from the respiration of human beings and animals; by evaporation from the skin; and by evaporation from plants. This aqueous vapour of the air, by condensing to small particles of water, forms clouds and mists, and, by further condensation to actual drops of water, produces rain; if when in the fine state of condensation it be frozen, snow is produced; whereas if rain be frozen during its transit to the earth, hail is produced.

The detection of aqueous vapour and the estimation of its amount in the air are effected by passing a measured volume of the air through a previously weighed chloride of calcium tube, when any aqueous

vapour in the air will be readily absorbed by the fragments of chloride of calcium, and the increase in weight of the tube at the end of the experiment will indicate the amount of aqueous vapour in the volume of air employed. The estimation of the amount of aqueous vapour is, however, more usually effected by physical methods, by determining the "dew-point."

(2) **Carbon dioxide.**—This gas, commonly known as carbonic acid gas, must be regarded as one of the essential constituents of the air, on account of the extremely important part it takes in the maintenance of vegetable life (*see* page 110), although, if allowed to accumulate in excessive quantities, it becomes an impurity of the atmosphere. It is derived from the respiration of human beings and animals, and from the combustion of fuel. The amount of carbon dioxide normally present in the air is very small, being 4 parts in 10,000 or .04 per cent., and an amount slightly in excess of this in the air of inhabited rooms must be regarded as an impurity, not so much on account of the carbon dioxide itself, as because it is derived from the respiration of human beings, and in the air exhaled from the lungs putrefiable organic matters are present that have a decidedly deleterious effect on the health of human beings breathing such air. When the carbon dioxide in the air of an inhabited room exceeds .06 per cent., these putrefiable organic matters become noticeable by smell, rendering the air stuffy or foul, but since these organic matters are extremely difficult to estimate, the determination of the amount of carbon dioxide present becomes a useful gauge of the foulness of the air. If the carbon dioxide be pure, 3 per cent. may be present without producing inconvenience. To detect carbon dioxide in the air, all that is necessary is to expose some lime-water to the atmosphere, when the presence of carbon dioxide is indicated by the

lime-water becoming turbid or milky, owing to the precipitation of carbonate of lime. The amount of carbon dioxide in the air may be estimated by:—

i. *Pettenkofer's method*.—A half-gallon bottle is filled with the air to be examined, and a measured quantity of baryta-water is poured into the bottle and thoroughly agitated with the air in it. The strength of the baryta-water is previously determined by ascertaining how much of a standard solution of oxalic acid is required to neutralise the same quantity of baryta-water as that introduced into the half-gallon bottle. If now the measured quantity of baryta-water that has been agitated with the half-gallon of air be filtered from the precipitated carbonate of barium, and its strength be determined by noting the quantity of standard acid that is required to neutralise it, it will be found to be deficient in a certain amount of baryta, which represents the quantity of baryta precipitated by the carbon dioxide in the half-gallon of air, from which the amount of carbon dioxide present in the air can be easily calculated.

ii. *Absorption with potash as already described*.—The quantity of carbon dioxide is so small in ordinary air that this method requires an apparatus specially adapted to show minute absorptions. Such an apparatus has been devised by Mr. Haldane, and is known by his name. It is represented in Fig. 18. G is a glass tube shaped like a pipette and having a capacity of about 20 c.c.; the stem is of very fine bore, and is graduated from 0 to 100 as shown; each division represents $\frac{1}{10000}$ th of the volume of the pipette from 0 to the tap B; the lower end of G is connected by rubber tubing to a reservoir of mercury M, which can be raised and lowered by the rack-and-pinion arrangement shown in sketch.

A is a comparison pipette, closed at the lower end, and connected above with the tap T.

A and G are placed side by side in a separate compartment, with glass front, containing water which can be agitated at will by blowing through the loose

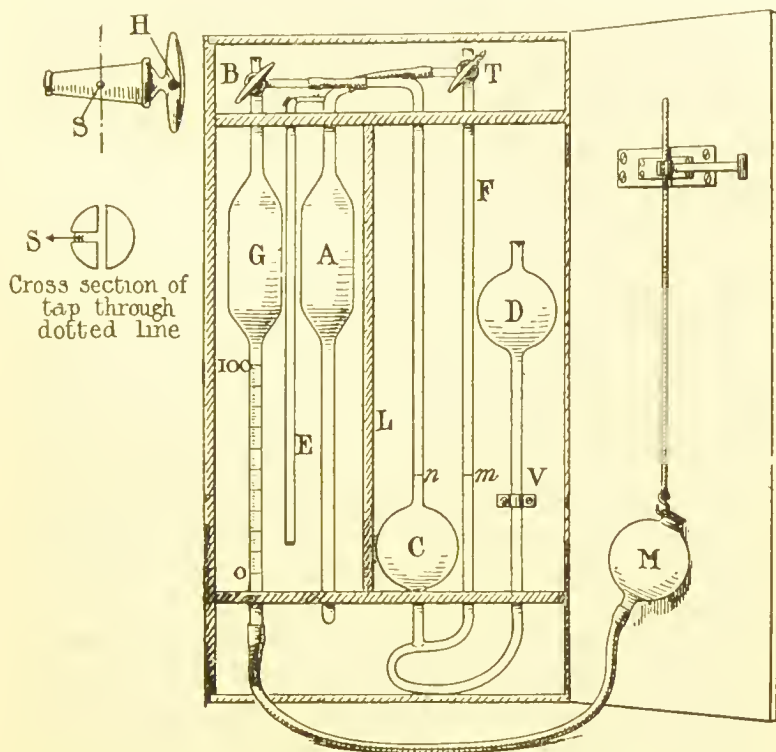


Fig. 18.—Haldane's apparatus for the estimation of small quantities of carbon dioxide, or other constituent, in air or gaseous mixtures generally, by absorption.

G, Graduated pipette; A, comparison pipette; M, mercury bulb and pressure tube attached; C, bulb containing caustic potash, or other suitable absorbent, and communicating with D and F; B and T, three way taps, shown on a larger scale at H and S.

tube E. The two pipettes can thus be kept at the same temperature.

D is a reservoir of caustic potash solution (20 per cent.), capable of being raised or lowered through

a clip V, and connected below by rubber tubing with the straight tube F and the bulbed tube c.

The structure of the taps B and T is a special feature of the apparatus, and is shown in cross section. The butt of the tap has a small distinguishing mark H on the side which corresponds to the outlets, and thus indicates the direction in which connections exist.

The apparatus should be left after use with the taps so turned that G and A are both in connection only with atmospheric air, thus:—



To use the apparatus, proceed as follows:—

Raise M to fill G with mercury; when full, turn B to cut off communication with air or c, thus:—



Turn T to connect A and F with atmosphere, thus:—



Adjust potash in F to mark *m* by raising or lowering D. Turn T to connect only A and F, thus:—



Lower M to convenient level for admission of air, and then turn B to connect G with air only, thus:—



When a convenient volume of air has entered, turn B to connect G with c only, thus:—



Stir the water thoroughly which surrounds G and A. Adjust potash in c to mark *n*, by raising or lowering M by means of the rack; read and record the level at which the mercury stands in the stem of G: suppose it is d_1 .

By raising M, force the air from G into c and keep it in contact with the potash there for a time.

Again stir the water thoroughly, adjust the potash in c to *n* by raising or lowering M with rack as before; read and record the level at which the mercury *now* stands in the stem of G: suppose it is d_2 .

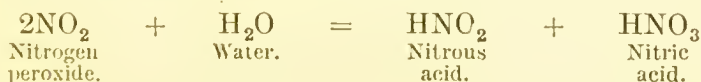
Then the air contains $d_2 - d_1$ parts of carbon dioxide by volume in 10,000, therefore the percentage of CO_2 by volume is $\frac{d_2 - d_1}{100}$. The absorption may

be repeated again and again on the same sample till two consecutive readings show no difference.

(3) The **argon group of gases** has already been discussed (page 131). To obtain them from air, atmospheric nitrogen, freed from its usual companions, oxygen, carbon dioxide, aqueous vapour, etc., was passed repeatedly over heated magnesium filings. Nitrogen combines with the metal to form magnesium nitride, leaving the inert gases alone. Their separation by fractional distillation is described in "Gases of the Atmosphere," to which reference has already been made. It may be well to add that, since its publication, helium has been liquefied at -268.5° or 4.5° on the absolute scale (*see* Chemical Society's Annual Reports, 1908, page 61).

(4) **Ammonia, in combination with nitrous and nitric acids**, appears to be present in very small and varying quantities, and is carried down, by solution in rain-water, to the soil. The presence of these acids has been explained as follows:—

Small quantities of nitrogen peroxide may be formed by direct union of the nitrogen and oxygen of the air during a thunderstorm, the nitrogen peroxide subsequently uniting with the moisture in the air to form nitrous and nitric acids.



The ammonia in the air, derived perhaps from the decomposition of nitrogenous organic matter (e.g. urea), combines with the acids to form ammonium nitrite and nitrate. On the other hand, it has been suggested that these salts might be formed

by the direct interaction of ozone and ammonia, thus :—



and



(5) **Hydrogen peroxide, H_2O_2 .**—In the preceding equations this substance is represented as a by-product of the reaction between ozone and ammonia.

3. OTHER SUBSTANCES THAT MAY BE PRESENT IN THE ATMOSPHERE

Ozone.—This gas is present in minute quantities in country air and in the vicinity of the sea, but not, as a rule, in the atmosphere of towns. Its production in the air and the means of detecting it have been previously described (*see* pages 110, 113).

Impurities. (1) *Nitrogen tetroxide and nitric acid.*—These have already been noticed, but may also be present in special localities owing to the neighbourhood of chemical works and factories.

(2) *Sulphur dioxide and sulphurous and sulphuric acids.*—Derived from the combustion of sulphur in coal, and from chemical works and factories.

(3) *Chlorine.*—From bleaching powder and other chemical works.

(4) *Sulphuretted hydrogen.*—Produced in the manufacture of coal gas, etc.

(5) *Carbon dioxide in excess.*—A product of respiration, combustion of coal, etc.

(6) *Carbonic oxide.*—From imperfect combustion of fuel.

(7) *Particles of soot.*—*See* 6.

(8) *Fungoid organisms and bacteria.*—From various sources.

CHAPTER V

OXIDES OF NITROGEN—NITRIC ACID— NITRATES—NITRITES

Nitrogen Monoxide—Nitrogen Dioxide—Nitrogen Trioxide
—Nitrogen Tetroxide—Nitrogen Pentoxide—Nitric
Acid—Nitrates—Nitrites

OXIDES OF NITROGEN

THERE are five compounds of oxygen and nitrogen,
viz :—

- N_2O Nitrogen monoxide, or nitrous oxide, or laugh-
ing gas.
 NO Nitrogen dioxide, or nitric oxide.
 N_2O_3 Nitrogen trioxide, or nitrous anhydride.
 NO_2 Nitrogen tetroxide, or nitric peroxide.
 N_2O_5 Nitrogen pentoxide, or nitric anhydride.

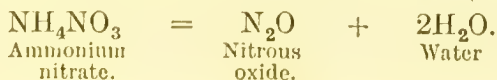
Of these oxides, the first four are gases, the last
is a white crystalline solid. The first two (N_2O
and NO) are colourless gases, the second two (N_2O_3
and NO_2) are both of a reddish-brown colour.

NITROGEN MONOXIDE

*Formula, N_2O ; molecular weight, 44; liquefies at
—90°; freezes at —104°; critical temperature, 37°.*

Also known as *nitrous oxide* and *laughing gas*.

Mode of preparation.—Nitrous oxide is ob-
tained by heating dry ammonium nitrate in a
flask, and collecting the gas over warm water, as
it is appreciably soluble in cold water (Fig. 19).



Properties.—The specific gravity of nitrous oxide is 22, and it is heavier than air; it is colourless and odourless, but has a slightly sweet taste. It is non-combustible. It is an endothermic compound, and is therefore decomposed without difficulty into its elements; the mixture so produced contains one-third of its volume of free oxygen,

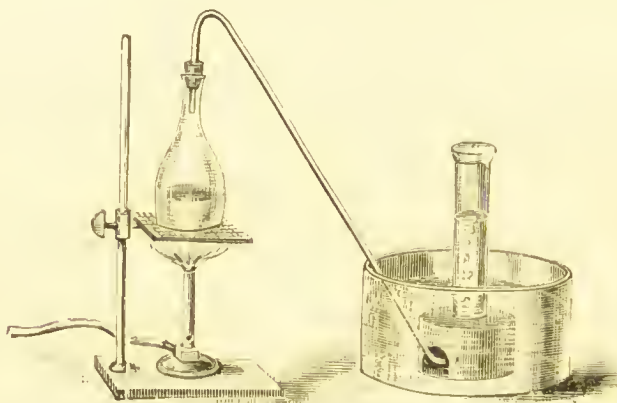


Fig. 19.—Preparation of nitrogen monoxide.

and therefore supports combustion very well. The pure compound, however, if undecomposed, does not support combustion.

Substances burning feebly, at a low temperature, are therefore extinguished when placed in the gas, but the same substances when burning strongly continue to do so. Phosphorus and sulphur, when well alight, burn brilliantly in laughing gas, because they are then able to decompose the gas into nitrogen and oxygen, and the free oxygen supports their combustion. The gas is fairly soluble in cold water, but considerably less so in hot. It is not a poisonous gas, although when inhaled in a pure state it produces insensibility, and is hence used for the painless performance of some minor operations.

If the administration of it be continued for too long a time, death from asphyxia will result. Nitrous oxide, prepared as above, usually contains some nitrogen peroxide and chlorine (the latter from the ammonium chloride present, as a rule, in commercial ammonium nitrate). To get rid of these dangerous impurities, the gas should be passed through potassium hydrate and ferrous sulphate solutions. The name of "laughing gas" is due to the fact that if nitrous oxide be inhaled mixed with air, a feeling of exhilaration is produced. Nitrous oxide, when brought in contact with the air, remains unchanged.

Tests.—The fact that nitrous oxide is a colourless gas, and does not change colour on exposure to the air, is sufficient to distinguish it from the other oxides of nitrogen; it may, however, be confounded with oxygen, since it rekindles a glowing splinter of wood. It can be readily distinguished from oxygen by two tests:

1. Adding a little nitric oxide, which will produce no effect with nitrous oxide, but will turn deep red with oxygen.

2. Burning a piece of potassium in some of the pure gas collected over mercury. Nitrous oxide liberates its own volume of nitrogen, and so the volume of the gas when cold will be unchanged; this method may therefore be employed to prove the composition of nitrous oxide; if, however, it is pure oxygen, the gas will disappear, as it combines with the potassium to form solid potassium oxide.

NITROGEN DIOXIDE

Formula, NO₂; molecular weight, 46; liquefies at -110°.

Also known as *nitric oxide*.

Modes of preparation.—1. Nitrogen dioxide

is most readily obtained by pouring slightly diluted nitric acid (of specific gravity 1.23) upon copper turnings, and collecting the gas over water (Fig. 20).

Of the nitric acid employed, only one-fourth furnishes the gas, the other three-fourths uniting with the copper to form copper nitrate, thus :

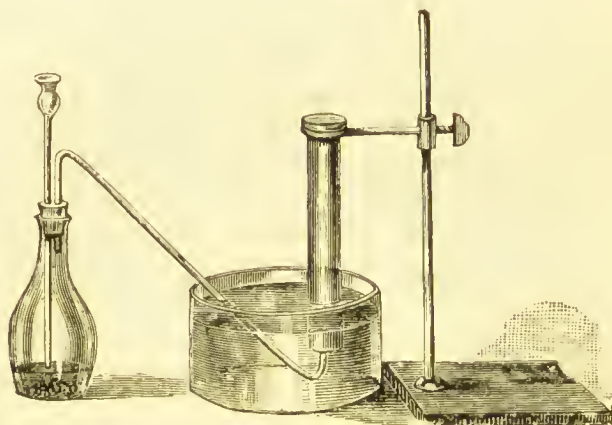
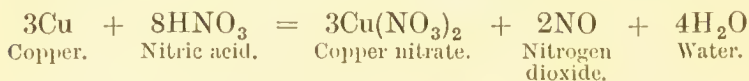
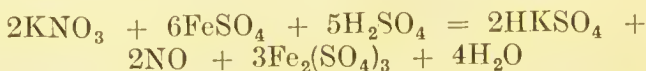


Fig. 20.—Preparation of nitrogen dioxide.

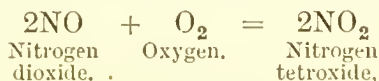
The gas thus prepared is never pure. It may be purified by means of ferrous sulphate solution (*see below*).

2. A much purer sample of the gas may accordingly be prepared by warming a mixture of potassium nitrate and ferrous sulphate with dilute sulphuric acid.

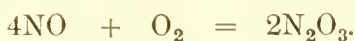


Properties.—The specific gravity of nitrogen dioxide is 15. As the specific gravity of NO is 15, its molecular weight must be 30, which indicates the formula NO. It is a colourless gas, but on exposure

to the air it becomes of a reddish-brown colour, due to its uniting with oxygen of the air to form either nitrogen trioxide or tetroxide. Thus, if in contact with excess of air, nitrogen tetroxide will be produced :



while with a smaller proportion of air we might have



As both N_2O_3 and NO_2 are easily soluble in water, they will be absorbed if the experiment is performed over water and the volume will be diminished. This diminution being due to the oxygen in the air, the amount of diminution is an index of the amount of oxygen, and therefore of the “goodness” of the air.

As regards the odour and taste of nitrogen dioxide nothing is definitely known, since it is impossible either to smell or taste it without its being brought into contact with air, in which case the smell and taste of either nitrogen trioxide or tetroxide would be observed. Nitrogen dioxide is non-combustible. A burning taper is extinguished when plunged into this gas, but if a more combustible substance, such as a brightly burning piece of phosphorus, be placed in the gas it decomposes the NO , liberating the oxygen, in which it continues to burn. It is practically insoluble in water, and it is a poisonous gas. If passed into a solution of ferrous sulphate it is absorbed, forming a dark brown solution which evolves nitric oxide when heated. Advantage is taken of this property in the ordinary test for nitrates, in which ferrous sulphate and sulphuric acid are added as reagents (page 156). It also furnishes a good method of obtaining a sample of *pure* nitric oxide.

Test.—Nitrogen dioxide is the only colourless gas that becomes of a reddish-brown colour on

exposure to the air; this is, therefore, a very simple and absolutely diagnostic test for the gas.

Composition.—If potassium be heated in a measured volume of pure NO over mercury, the volume of the residual gas will, when cold, be reduced to one-half, and will be found to be nitrogen. This gas therefore contains only half its volume of nitrogen.

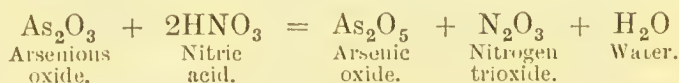


NITROGEN TRIOXIDE

Formula, N₂O₃; molecular weight, 76.

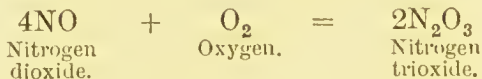
Also known as *nitrous anhydride*.

Modes of preparation.—1. Nitrogen trioxide is best prepared by the action of nitric acid, diluted with half its volume of water, at 70°, on white arsenic (arsenious oxide), when the higher oxide of arsenic is produced, a reddish-brown gas being evolved, thus:



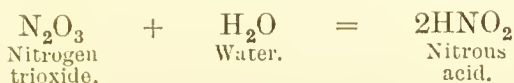
2. Nitrogen trioxide can be obtained, though not in a pure state, by the action of nitric acid, with heat, on starch.

3. Nitrogen trioxide may also be prepared by bringing nitrogen dioxide into contact with a limited amount of oxygen, or of air, thus:

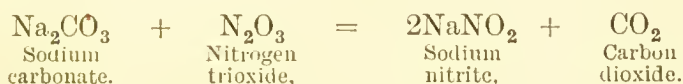
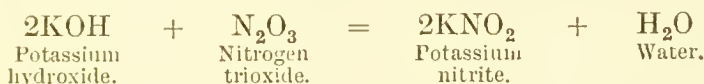


Properties.—If the reddish fumes obtained by any of the above reactions be cooled to -18°, a blue liquid is obtained, which is believed to be liquid N₂O₃. There seems to be, however, considerable doubt as to the existence of *gaseous* N₂O₃, the reddish

fumes mentioned above being principally a mixture of NO and NO₂. When passed into water the red fumes dissolve, uniting with the water to form nitrous acid (page 159), a very unstable body.



Similarly, if passed into a solution of an alkali or of an alkaline carbonate, it will form a nitrite of the alkali metal, thus :

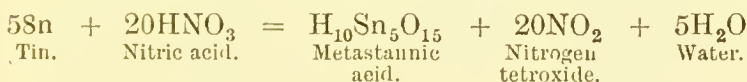


NITROGEN TETROXIDE

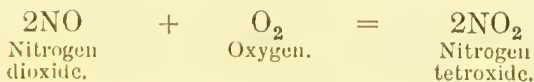
Formula, NO₂ ; molecular weight, 46 (but see page 152) ; liquefies at +22° ; freezes at -10°.

Also known as *nitric peroxide*.

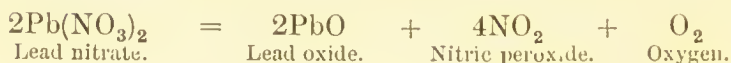
Modes of preparation.—1. The simplest way of obtaining nitrogen tetroxide, for experimental purposes, is by the action of strong nitric acid on the metal tin, when a violent action takes place with copious evolution of the gas and the production of a white powder, metastannic acid.



2. Nitrogen tetroxide may be obtained by mixing nitrogen dioxide with a sufficiency of oxygen, or of air.



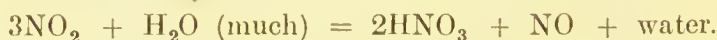
3. It is evolved when dry lead nitrate is heated.



Properties.—The specific gravity of nitrogen tetroxide is 23, and it is therefore heavier than air. Its specific gravity, however, varies with the temperature. Thus, just above its boiling-point (22°), the specific gravity is 38.3; at 140° it is 23; so that both molecules, NO_2 and N_2O_4 , seem to exist. These apparent anomalies have already been discussed on page 46, to which the student is advised to refer. This oxide possesses a reddish-brown colour, a strong odour, and an unpleasant acid taste. It is non-combustible; it is a poisonous gas, and undergoes no change when brought into contact with the air. It dissolves readily in water, producing a mixture of nitrous and nitric acids in the cold, according to the equation:—



But with *hot* water, only *nitric* acid appears to persist, the equation being—



Similarly, if passed into a solution of an alkali or of an alkaline carbonate, it will form a mixture of a nitrite and a nitrate of the alkali metal, thus:—



NITROGEN PENTOXIDE

Formula, N_2O_5 ; molecular weight, 108; melts, 30° ; boils, 45° (with decomposition in both liquid and gaseous states).

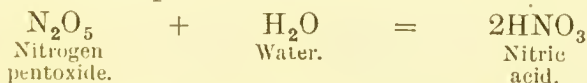
Also known as *nitric anhydride*.

Mode of preparation.—Nitrogen pentoxide, or nitric anhydride, is prepared by passing a stream of chlorine gas over solid nitrate of silver contained in a glass tube and gently heated, when the chlorine unites with the silver to form silver chloride, and the vapour of nitric anhydride and oxygen are evolved, the nitric anhydride condensing as a white crystalline solid in the cool part of the tube, and the oxygen escaping.



If too much heat is employed, the nitric anhydride is decomposed with explosive force.

Properties.—Nitrogen pentoxide is the only solid oxide of nitrogen; it is a white crystalline substance. When placed in water it forms nitric acid.



It sometimes decomposes spontaneously at ordinary temperatures.

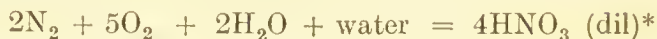
All the oxides of nitrogen are decomposed when they are passed over red-hot copper. By this reaction, if the copper be weighed and the nitrogen collected, their composition can be determined.

NITRIC ACID

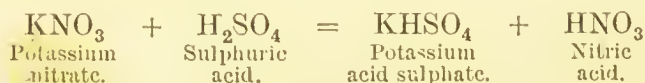
*Formula, HNO_3 ; molecular weight, 63;
commences to boil at 86° .*

Nitric acid is formed from the nitrogen and

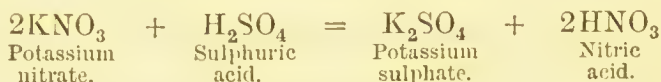
oxygen of the air in presence of moisture and the silent electric discharge, thus :



Mode of preparation.—The preparation of nitric acid illustrates a method very often employed for the preparation of an acid from its salts. The salt is placed in a retort together with strong sulphuric acid. On the mixture being heated the acid distils over and is collected in a well-cooled flask or “receiver.” No cork, or rubber connection, should be used in the apparatus, as both these substances are acted on by the strong acid. One of the natural nitrates, potassium nitrate or sodium nitrate, is employed, and according to the amount of sulphuric acid and the heat used, an acid sulphate or a normal sulphate of the alkali metal will be left behind in the retort. Thus, if the sulphuric acid be in excess, an acid sulphate is formed :



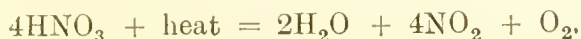
At a higher temperature, if the nitrate be in excess, a normal sulphate is formed :



Properties.—Nitric acid, if pure, is a colourless liquid, fuming on exposure to the air, and possessing an irritating smell. Commercial nitric acid consists of 70 per cent. of nitric acid, the remaining 30 per cent. being water, and it is of specific gravity 1.42. Pure nitric acid is of specific gravity 1.52, and is a somewhat unstable body, soon decomposing under

* See Chem. Society's Annual Reports, 1906, p. 53.

the influence of heat and light into water, nitrogen, peroxide and oxygen, thus :



The NO_2 dissolves in the undecomposed nitric acid, giving it the yellow colour often seen in the strong nitric acid on the laboratory shelves. On boiling the yellow acid, the NO_2 is expelled and the acid becomes colourless, but weaker, till it finally attains a strength of 68 per cent. and a boiling-point of 121° . This is the acid of constant composition to which all others rise or fall on being boiled. *Aqua-fortis* is an old name for nitric acid, given to it on account of its property of acting on most of the metals; the only common metals not acted on by nitric acid are gold, platinum, and aluminium. A general account of the action of nitric acid on the metals has already been given (page 74), and is of great importance. A mixture of two parts of nitric acid to four parts of hydrochloric acid is known as *aqua regia*, on account of its property of dissolving gold, the "king of metals." A commercial article known as *yellow* or *fuming nitric acid*, which contains dissolved nitrogen peroxide, is made by distilling potassium nitrate and strong sulphuric acid in the proportions to form the neutral potassium sulphate, and using a higher temperature than is employed in the manufacture of the ordinary acid. Nitric acid corrodes and stains the skin and articles of clothing yellow; the colour is not removed but intensified by the application of solution of ammonia. Strong nitric acid is a powerful corrosive and irritant poison. Containing as it does more than 76 per cent. of oxygen, it forms, as might be expected, a powerful oxidising agent (page 76). It is constantly employed in that capacity to convert ferrous salts into ferric (*see* page 157).

Impurities.—The acidum nitricum of the B.P.* is the acid of constant composition already mentioned. The official description requires that it should leave no residue when a few cubic centimetres are evaporated to dryness, and also should not respond to the tests for lead, copper, arsenic, iron, chlorides, bromates, iodates, and sulphates.

Tests.—1. A solid **nitrate** heated with strong sulphuric acid and a small strip of copper evolves brown fumes.

2. A solid **nitrate** mixed with a fragment of brucine strikes a crimson colour on addition of cold, strong sulphuric acid.

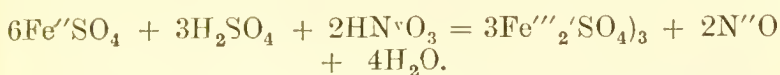
3. All **nitrates** are soluble in water, and their presence in the solution is detected as follows: To a small portion of the solution in a test-tube add about the same volume of a fresh solution of ferrous sulphate; incline the tube, and pour strong sulphuric acid slowly down the side till a layer of the heavy acid is formed beneath the mixture; a deep brown ring will appear at the junction if a nitrate is present. The tube and its contents should be kept cold and undisturbed throughout the test till the ring is plainly seen. On then shaking the tube and applying heat, a gas (NO) is expelled, and the liquid becomes clear and almost colourless. This behaviour is useful in confirming the presence of a nitrate, as a very similar dark ring is sometimes produced when the test is applied, which is due to the charring of a carbonaceous substance like sugar, or to the liberation of iodine from an iodide. In these two cases, however, the dark effect can be obtained by sulphuric acid alone. On that account the acid and ferrous sulphate are sometimes added in the reverse order to that which is recommended above; this is a matter which may be left to the personal preference

* British Pharmacopœia.

of the analyst when he has had experience of both. The student must, however, be able to *explain* this test, as well as perform it; the brown ring obtained is really due to three distinct reactions:

(1) Strong sulphuric acid liberates nitric acid from the nitrate, as in the preparation of nitric acid (page 154).

(2) The free nitric acid oxidises some of the ferrous sulphate to ferric sulphate and is itself reduced to nitric oxide in the process.



The valency of the iron is increased from two to three (oxidation), and the valency of the nitrogen is diminished from five to two (reduction) (*see* page 76).

(3) If the solution remains cold and undisturbed, the nitric oxide does not escape, but dissolves in some of the unchanged ferrous sulphate, and thus forms the dark-brown substance. The composition of this substance must naturally depend somewhat upon temperature and pressure, but in ordinary circumstances it may be represented by the formula $\text{NO}, 2\text{FeSO}_4$.

Estimation.—The free acid is estimated by the usual volumetric methods (page 598). Nitrates can be estimated by converting them into ammonia by nascent hydrogen. The ammonia is then distilled off and estimated by the Nessler test (*see* Ammonia, page 165). The hydrogen can be produced by adding to the solution of the nitrate a zinc-copper couple; this is made by immersing a clean strip of zinc foil in a solution of copper sulphate.



The method is employed for the estimation of nitrates in water analysis.

NITRATES

Nitrates occurring in nature are produced by the oxidation of organic nitrogenous bodies, the resulting nitric acid becoming neutralised by contact with salts of the alkali or alkaline earth metals. In many, if not in all, cases this oxidation of the nitrogen of organic nitrogenous bodies to nitric acid is brought about by the influence of a ferment called the "nitrifying ferment," which may exist in the soil or in water. The nitre or saltpetre (KNO_3) formed in the surface soil of various parts of India is produced by the oxidation of organic nitrogenous bodies (especially the excreta of animals and human beings), under the influence of the nitrifying ferment and the tropical heat, in a soil rich in potassium salts. The action of this ferment ceases when it is exposed to the light.

The small quantities of nitrates (nitrates of calcium and magnesium) that may be present in well-waters or river-waters which have been contaminated with sewage are similarly produced by oxidation of the nitrogenous matters of the sewage, under the influence of the ferment, to nitric acid, and subsequent neutralisation of this acid by the carbonate of calcium or magnesium in the water.

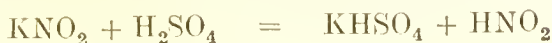
Potassium *nitrate* when strongly heated parts with one-third of the oxygen and leaves the *nitrite* :



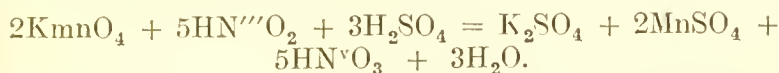
NITRITES

As already stated (page 151), nitrous acid itself is a very unstable body and cannot be said to be known in a pure state. Stable salts of the acid are, however, well known; the potassium and ammonium salts have already been employed in the preparation of nitrogen (page 129). When their aqueous solu-

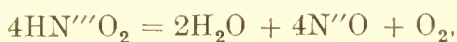
tions are acidulated with *dilute* sulphuric acid the unstable nitrous acid is liberated, thus :



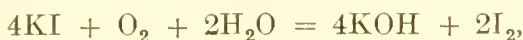
Tests.—These solutions (1) discharge the colour of a potassium permanganate solution, owing, we must suppose, to the reducing action of the nitrous acid which borrows oxygen from the permanganate and becomes nitric acid, thus :



The solutions (2) liberate iodine from a solution of potassium iodide. As this is characteristic of *oxidising* agents, we suppose that the nitrous acid here decomposes, thus :



and that the liberated oxygen decomposes the potassium iodide thus :—



the caustic potash combining with free acid.

The solutions (3) give a dark brown colour to solution of ferrous sulphate, owing, we suppose, to the solution of the NO (formed as in (2)) in the ferrous sulphate, and consequent formation of a dark-brown compound similar to that present in the brown ring test for *nitrates* (page 157). In that case, however *strong* sulphuric acid was, and must be, used. Here *dilute* sulphuric acid only is used. By this and the foregoing tests, **nitrites** are easily distinguished from **nitrates**, and also from other salts. Test (2) is rendered particularly delicate by the addition of a few drops of cold starch solution with which the free iodine forms a strong blue colour. In this form the test is constantly employed for the detection of **nitrites** in natural waters.

CHAPTER VI

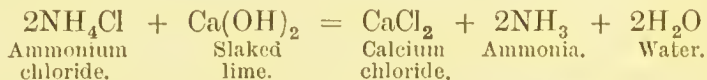
AMMONIA AND AMMONIUM SALTS

Ammonia—Ammonium and its Salts—Unstable Compounds

AMMONIA

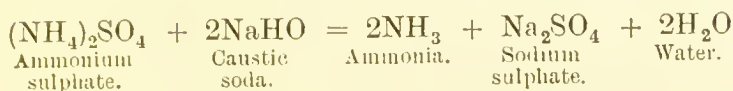
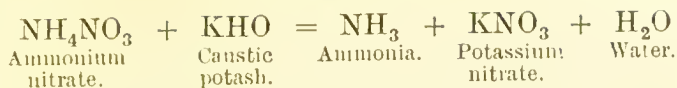
Formula, NH_3 ; molecular weight, 17; liquefies at -40° ; freezes at -77° ; critical temperature, 131° .

Modes of preparation.—1. The method most often employed to obtain the base from a salt is to act on the salt, either in the dry state or in solution, with another base, which for some chemical reason can combine with the acid of the salt in preference to the original base, this being therefore displaced and set free. It has already been stated that ammonia functions as a base, and we accordingly find that it is prepared by acting on an ammonium salt by a suitable base. The hydroxide of potassium, sodium, or calcium is generally employed. Ammonia gas is therefore conveniently prepared by heating a mixture of dry ammonium chloride and slaked lime ($\text{Ca}(\text{OH})_2$):



The ammonia gas cannot be collected over water, on account of its extreme solubility, but may be collected over mercury, or by upward displacement (*see* Fig. 21), on account of its being lighter than air.

2. Ammonia may also be prepared by heating ammonium salt with caustic potash or caustic soda :



3. Ammonia is formed by the action of dilute nitric acid on the metal zinc; the action is probably

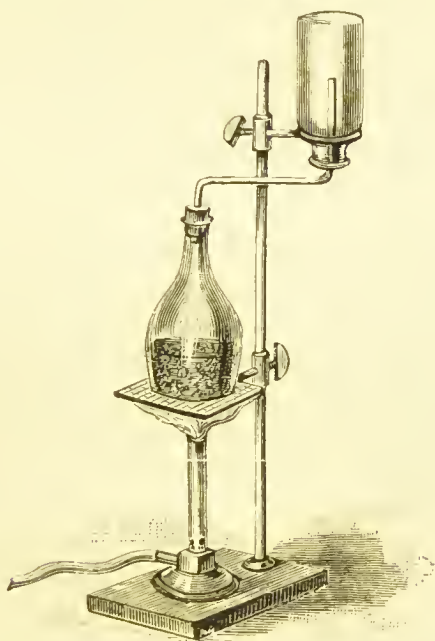
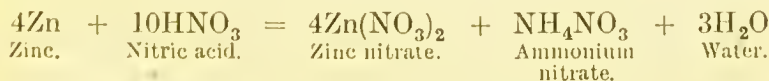


Fig. 21.—Preparation and collection of ammonia gas.

similar to the reduction of nitrates to ammonia by the nascent hydrogen from the zinc-copper couple (page 157) :



In this case, however, the ammonia is not evolved, but unites with some of the nitric acid to form ammonium nitrate. It may be subsequently obtained

from the salt by heating with a caustic alkali, as already described.

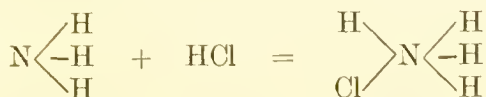
4. Ammonia is also obtained by the action of dry heat without contact of air (destructive distillation) on various organic nitrogenous substances of both animal and vegetable origin. Thus, by the destructive distillation of the horns of animals, ammonia may be obtained; hence the derivation of the old name, "spirit of hartshorn," applied to solution of ammonia. Also during the destructive distillation of coal, about half of the nitrogen unites with some of the hydrogen of the coal to form ammonia, which is ultimately found dissolved in the light "tar liquor" floating on the top of the condensed tar.

5. Ammonia is also formed during the spontaneous decomposition of moist animal matter, and during the putrefaction of urine.

6. By heating many nitrogenous bodies with strong caustic alkalies, the nitrogen of the organic bodies is converted into ammonia. Advantage is taken of this fact in determining the proportion of nitrogen present in such bodies, by ascertaining the amount of ammonia produced, when a weighed quantity of the substance is heated with soda-lime.

Properties.—The specific gravity of ammonia is 8.5, and it is lighter than air; it is a colourless gas, with a characteristic strong pungent odour and alkaline taste; it is feebly combustible, not catching fire in air, but in oxygen it burns with a pale yellowish or greenish-yellow flame; it also burns in air when mixed with hydrogen or coal gas, some nitric acid being formed; it does not support combustion. It is the most soluble of all gases in water; 1 volume of water dissolves over 800 volumes of the gas at ordinary temperatures. It is very easily liquefied

by pressure, since at ordinary temperatures under a pressure of seven atmospheres it becomes liquid. Ammonia is an unsaturated compound (page 23), and readily forms salts by addition, thus :



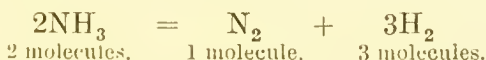
or



The salts are saturated compounds, as the nitrogen in these is employing its maximum valency.

The gas may be dried, when necessary, by passing it over quicklime (CaO). If inhaled in large quantities and in the pure state, it is a poison, on account of its irritating action on the mucous membrane of the respiratory passages.

Composition.—Ammonia is composed of 1 volume of nitrogen united with 3 volumes of hydrogen, the 4 volumes being condensed, as a result of the union, to 2 volumes ; therefore, if ammonia gas is decomposed into its elements its volume becomes doubled, thus :



From which it is seen that 2 molecules of ammonia gas produce 4 molecules of the mixture of nitrogen and hydrogen, and, since the molecules of all gases occupy the same bulk, therefore ammonia gas becomes doubled in bulk when it is resolved into its elements. This decomposition of ammonia gas into its elements can be effected at a high temperature, or by passing electric sparks for some time through the gas confined in a eudiometer over mercury (Fig. 22).

If after this decomposition into its elements an

excess of oxygen be added and the mixture exploded, a great diminution in bulk takes place, owing to the hydrogen uniting with half its volume of oxygen to form a minute drop of water. Two-thirds of this diminution give the hydrogen present in the 25 c.c. of ammonia. Thus :

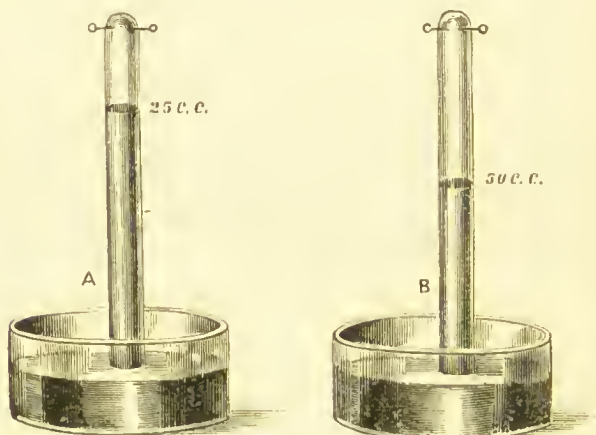


Fig. 22.—A, ammonia gas before the passage of electric sparks ; B, after passage of electric sparks for some time (volume doubled).

25 cc. of NH_3 on passing sparks = 50 c.c. of $\text{N}_2 + \text{H}_2$, add 30 c.c. of oxygen \therefore 80 c.c. of $\text{N}_2 + \text{H}_2 + \text{O}_2$ are present ;

after explosion, the residual gas measures 23.8 c.c.

\therefore diminution = $80 - 23.8 = 56.2$ c.c. ;

multiplying by $\frac{2}{3}$ we get 37.5 c.c. of H_2

and $(50 - 37.5) = 12.5$ c.c. of N_2 in 25 c.c. of NH_3 .

\therefore 1 volume of N_2 and 3 volumes of H_2 combine to form 2 volumes of NH_3 .

Tests.—1. The odour of the gas constitutes a fairly delicate test.

2. Dense white fumes are produced on inserting a rod moistened with strong hydrochloric acid into a jar or tube of the gas.

3. Moistened red litmus paper is turned blue when brought in contact with the gas.

4. The most delicate test for small quantities of ammonia in solution, as in a drinking-water, is the "Nessler test"; this consists in adding to the water some Nessler reagent (*see* page 310), when a reddish-brown colour or precipitate is produced, according to the amount of ammonia present. This test will detect 1 part by weight of ammonia in 5,000,000 of water. Up to a certain strength, the *intensity* of the colour produced indicates the *quantity* of ammonia present.

AMMONIUM AND ITS SALTS

The radicle ammonium (NH_4) has never been isolated, nor has the molecule $(\text{NH}_4)_2$. The latter, however, has been obtained in the form of an amalgam with mercury, by placing sodium amalgam in a strong solution of ammonium chloride, when the ammonium takes the place of the sodium, and a light, bulky amalgam with a metallic lustre is obtained.

This ammonium amalgam is, however, very unstable, and in the course of a few minutes is resolved into free mercury, with escape of ammonia and hydrogen gases.

Sources of the ammonium salts.—1. The ammonium salts of commerce are principally prepared directly or indirectly from the *ammoniacal tar liquor* of the gasworks (*see* page 162); this contains, in solution, free ammonia, and on distillation, neutralisation with hydrochloric acid and subsequent concentration of the liquid by evaporation, crystals of ammonium chloride are obtained. 2. The boric acid of volcanic origin obtained in Tuseany (*see* page 219) is accompanied by ammonium salts, and on submitting the crude boric acid to heat with carbonate of soda, a very pure carbonate of ammo-

num (the so-called volcanic carbonate of ammonium) volatilises and condenses.

3. As mentioned on page 162, solution of ammonia (spirit of hartshorn) was formerly prepared by the destructive distillation of the horns of animals.

4. The excreta of some animals, such as camels and serpents, contain large quantities of ammonium salts; and by heating the excreta with sodium chloride (common salt), ammonium chloride volatilises and can be condensed in the solid form.

AMMONIUM SALTS

Ammonium chloride (NH_4Cl). Also known as *sal ammoniac*. As previously described, this is obtained from the ammoniacal coal-tar liquor of the gasworks. Its preparation from ammonia solution and hydrochloric acid is described on page 575.

Description.—Small, colourless, crystals, when purified, but the commercial salt is seen in tough, fibrous lumps.

Ordinary impurities.—Carbonate, nitrate, sulphate, sulphocyanide, non-volatile matter.

Ammonium carbonate ($\text{N}_4\text{H}_{16}\text{C}_3\text{O}_8$).—Prepared by heating a mixture of solid ammonium chloride and chalk (calcium carbonate), when the ammonium carbonate sublimes as a white solid. This, the commercial ammonium carbonate, is not the normal carbonate, but consists of a mixture of two molecules of the bicarbonate of ammonium (NH_4HCO_3) with one molecule of the carbamate of ammonium ($\text{NH}_4\text{NH}_2\text{CO}_2$), thus:



By dissolving this commercial carbonate in water, the carbamate unites with the elements of water to form the normal carbonate, thus:



Then, if some solution of ammonia be added to this solution, the bicarbonate is also converted into the normal carbonate, thus :



So that to prepare a solution of the normal ammonium carbonate, such as is employed as a test-reagent, it is necessary to dissolve the commercial carbonate in water, and then to add some solution of ammonia.

Description.—White, crystalline masses, which smell of ammonia.

Ordinary impurities.—Chloride, sulphate ; tarry or non-volatile matter.

Ammonium nitrate (NH_4NO_3).—Prepared by neutralising nitric acid with ammonium carbonate, or with solution of ammonia.

Ammonium bromide (NH_4Br).—Prepared by neutralising hydrobromic acid with ammonium carbonate, or with solution of ammonia.

Description.—Small, colourless crystals, volatile with heat and soluble in water.

Ordinary impurities.—Chloride, nitrate, sulphate, bromate, iodide ; lead, iron ; non-volatile matter.

Ammonium sulphide ($(\text{NH}_4)_2\text{S}$).—Prepared by saturating solution of ammonia with sulphuretted hydrogen gas.



Ammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$.—Prepared by neutralising orthophosphoric acid with solution of ammonia.

Description.—Colourless crystals soluble in water which becomes alkaline; the aqueous solution, on boiling, evolves ammonia.

Ordinary impurities.—Chloride, sulphate; other metals.

Ammonium acetate, citrate, oxalate, and benzoate are made by neutralising the respective acids with ammonium carbonate, or with solution of ammonia.

Tests.—1. If a solution of an ammonium salt be heated with caustic potash or caustic soda, ammonia gas will be evolved, which can be recognised by its odour, by its turning moistened red litmus paper blue, and by the white fumes produced when a glass rod moistened with strong hydrochloric acid is brought near it.

2. If to a solution of an ammonium salt some Nessler reagent be added, a reddish-brown colour or precipitate will be produced. This reaction is only used for detecting very minute quantities of ammonia.

Other compounds of nitrogen and hydrogen exist, but they are somewhat unstable.

Hydroxylamine (NH_2HO) can be obtained in solution by the action of nascent hydrogen on nitric acid. It has been prepared in the pure state, when it forms a colourless, odourless, crystalline solid, which explodes when heated; it is a powerful reducing substance.

Hydrazine (N_2H_4).—This is a liquid solidifying at -1° ; it has a dreadful odour, and fumes violently in the air.

Hydrazine hydrate ($\text{N}_2\text{H}_4\text{H}_2\text{O}$) is a colourless fuming liquid which attacks and corrodes glass, cork, india-rubber, etc. It is a reducing substance, and forms salts with acids ($\text{N}_2\text{H}_4\text{HCl}$).

Azoimide or hydrazoic acid (N_3H) is a liquid

boiling at 37° , has a fearful odour, is very soluble in water, forming an acid solution resembling hydrochloric acid: thus, it dissolves iron and magnesium, evolving hydrogen, gives a white precipitate with silver nitrate, and forms dense white fumes with ammonia. It explodes with great violence when heated.

CHAPTER VII

HALOGEN ELEMENTS

Halogen Elements—Chlorine—Hydrogen Chloride—Nitrohydrochloric Acid—Compounds of Chlorine with Oxygen—Oxyacids of Chlorine

THE halogen elements—viz. chlorine, bromine, iodine, and fluorine—are four elements that are closely allied to one another in their properties. With metals they all form compounds analogous to sea-salt, hence the derivation of the term halogen (from ἅλς, sea-salt; γεννάω, I produce). None of them occurs free in nature.

As frequently happens in the case of allied elements, the one of least atomic weight (fluorine) is more singular in many respects than any of the others. The last three, in fact, form a favourite triad often used to illustrate the gradation of properties, physical and chemical, that goes hand in hand in their case with gradation of atomic weight. As in atomic weight, so in all its familiar properties, the liquid bromine stands half-way between gaseous chlorine and solid iodine.

I. CHLORINE

Symbol, Cl; molecule, Cl₂; heptad, but uses only monad valency in chlorides and hypochlorites (see page 64); atomic weight, 35.5; molecular weight, 71; liquefies at -34° ; freezes at -102° ; critical temperature, 146° .

Chlorine occurs in nature combined with metals

as chlorides, of which sodium chloride, *sea-salt* or *rock-salt*, is the most common. The name chlorine is derived from $\chi\lambda\omega\rho\acute{o}\varsigma$, green, on account of the greenish-yellow colour of the gas.

Modes of preparation.—1. Chlorine is most readily prepared by heating a mixture of strong hydrochloric acid and manganese dioxide (black

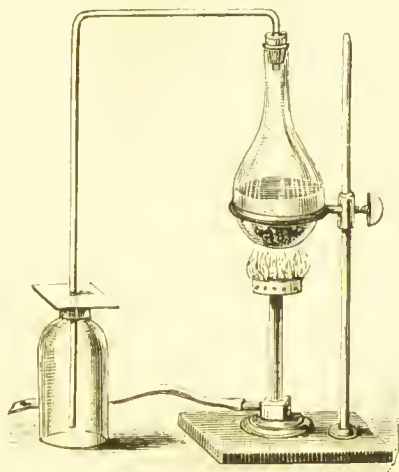


Fig. 23.—Preparation and collection of chlorine.

oxide of manganese), and collecting the gas by downward displacement of air (Fig. 23).

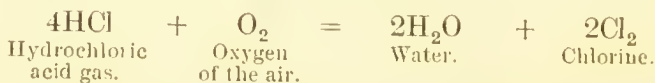


2. Chlorine may also be prepared by heating a mixture of common salt, manganese dioxide, and sulphuric acid.



In a similar way, chlorine may be obtained by the action of manganese dioxide and sulphuric acid on any metallic chloride.

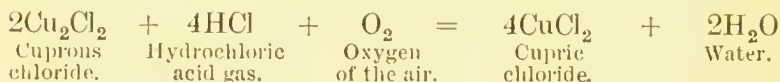
3. By passing a mixture of hydrochloric acid gas and air over red-hot bricks, chlorine is liberated ; by this method the chlorine obtained is necessarily mixed with the nitrogen of the air, an admixture of but little importance when the chlorine is to be used for manufacturing purposes.



4. Deacon's process for the manufacture of chlorine consists in passing a mixture of hydrochloric acid gas and air over heated fragments of pumice stone saturated with cupric chloride. The cupric chloride is decomposed into cuprous chloride, evolving one-half of its chlorine.



The cuprous chloride is then reconverted into cupric chloride by means of chlorine, which is liberated from the hydrochloric acid gas by the oxygen of the air.



The cupric chloride then again becomes reduced to cuprous chloride with evolution of half its chlorine, and so on.

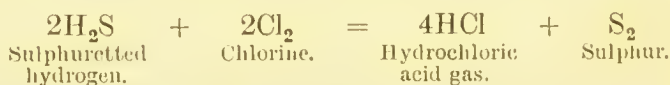
5. Chlorine may be obtained by the electrolysis (page 103) of hydrochloric acid, or of a solution of salt, using electrodes of gas-carbon ; equal volumes of chlorine and hydrogen are evolved, the chlorine being set free at the anode, and the hydrogen or sodium (immediately converted by the water into sodium hydrate and hydrogen) at the kathode.

Properties.—The specific gravity of chlorine is 35.5 ; it is a heavy gas, being $2\frac{1}{2}$ times heavier than air. It has a greenish-yellow colour, a very unpleasant suffocating odour, and a disagreeable taste. It is non-combustible, as chlorine will not combine directly with oxygen, but, in an atmosphere of hydrogen, chlorine will burn with a pale livid flame, producing hydrochloric acid ; and conversely, hydrogen will burn in an atmosphere of chlorine. Chlorine is a supporter of combustion in a limited sense only ; if a burning body contains hydrogen, then it will continue to burn in chlorine with a feeble flame, the chlorine uniting with the hydrogen to form hydrochloric acid, but not uniting with the carbon of the burning body. Thus, if a lighted candle be lowered into a jar of chlorine, the candle will continue to burn with a reddish flame, and all the carbon will be set free as a dense smoke. A piece of glowing charcoal will not burn in chlorine, since it contains no hydrogen. If a piece of paper saturated with oil of turpentine ($C_{10}H_{16}$) be thrown into a jar of chlorine, the turpentine catches fire from the heat produced by the rapid union of the chlorine with the hydrogen, but all the carbon is set free as dense smoke.

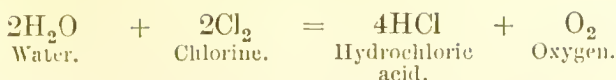
Chlorine is also a supporter of combustion as regards the following bodies : A piece of phosphorus catches fire when introduced into chlorine, forming the pentachloride of phosphorus (PCl_5). Chlorine will also combine with all metals, forming metallic chlorides ; and if some metals in a fine state of division (such as powdered antimony) be thrown into a jar of chlorine they will ignite spontaneously, from the heat produced by the intensity of the union of the chlorine with the metal. Chlorine is soluble in water, 1 volume of water dissolving about $2\frac{1}{2}$ volumes of the gas ; it must, therefore, be collected over hot

water, or by displacement, not over mercury, since it would combine with that metal. When submitted to a pressure of six atmospheres, at ordinary temperatures, it is condensed to a yellow liquid.

Chlorine is a poisonous gas, acting as a powerful irritant to the mucous membrane of the respiratory passages. Chlorine is also an important bleaching and disinfecting agent; it bleaches all vegetable colours in presence of moisture, acting in two ways: partly by uniting with the hydrogen of the dye and replacing it by chlorine, and so forming a colourless substitution product; and partly by uniting with the hydrogen of the water and liberating oxygen, which in the nascent state oxidises and destroys the colouring matter. Chlorine does not bleach mineral colours. As a disinfecting agent, chlorine acts as a powerful germicide, but its unpleasant odour and irritating properties when inhaled prevent its general use as a disinfectant. Chlorine is also a deodoriser, acting in virtue of its affinity for hydrogen, by uniting with the hydrogen of bad-smelling gases and so decomposing them; for instance, if chlorine be brought into contact with sulphuretted hydrogen, hydrochloric acid is formed and sulphur precipitated.



The two most marked chemical properties of chlorine are: (a) its property of combining with hydrogen; (b) its property of uniting with metals. Several instances of both these properties have been given; a further illustration of the first-mentioned one may be cited here. So great is the power of chlorine of uniting with hydrogen, that if chlorine water be simply exposed to direct sunlight it is decomposed, the chlorine uniting with the hydrogen of the water and setting free the oxygen.



If a mixture of equal volumes of hydrogen and chlorine be exposed to sunlight, the mixture will explode.

Tests.—1. The colour, the odour and the fact that a piece of moistened litmus paper (blue or red) is bleached by the gas, constitute very fair tests for chlorine.

2. The most delicate test for chlorine is based upon the fact of its liberating iodine from iodide of potassium, the liberated iodine in contact with starch forming a blue compound. If a piece of blotting-paper be dipped in a mixed solution of potassium iodide and starch paste, and then be brought in contact with chlorine, it is turned a blue colour. (N.B.—This reaction is also produced by ozone, and by nitrogen trioxide and peroxide; see page 113).

HYDROGEN CHLORIDE

Formula, HCl; molecular weight, 36.5; liquefies at -102° ; freezes, at -112° ; critical temperature, 52° .

A solution of this gas is known as *muratic acid*, *hydrochloric acid*, and *spirit of salt*. The latter name is applied to an impure form of the acid, which is of a yellowish colour from contamination with ferric chloride; it also generally contains arsenic as an impurity, derived from the impure sulphuric acid that is used in its manufacture.

Modes of preparation.—1. Hydrogen chloride is most easily prepared by heating a mixture of sodium chloride (common salt) and sulphuric acid (sp. gr. 1.47).



The hydrogen chloride is given off as a gas, and after washing it through a small quantity of water, it is conveyed into water contained in a bottle kept cool by being surrounded with water (Fig. 24). It readily dissolves in the water, and this solution constitutes the hydrochloric acid of commerce.

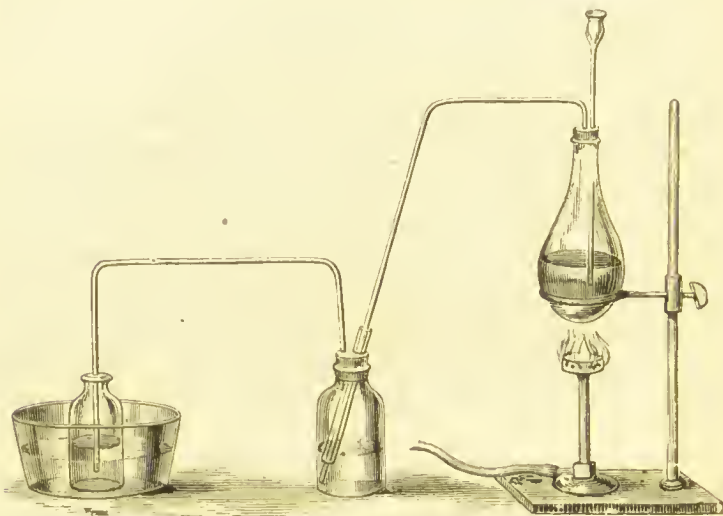


Fig. 24.—Preparation of hydrochloric acid.

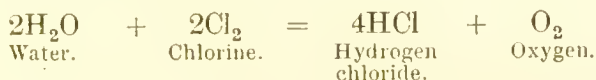
2. In a similar manner, hydrochloric acid may be prepared by heating sulphuric acid with any metallic chloride.

3. Hydrogen chloride may be prepared by mixing together equal volumes of hydrogen and chlorine, and exposing the mixture of gases to diffused light, when they combine quietly; if the mixture be exposed to strong sunlight, or if a light be applied, the two gases unite suddenly with an explosion. The volume of hydrochloric acid gas formed is exactly equal to the volumes of the constituents; for



One molecule of hydrogen unites with one molecule of chlorine to produce two molecules of hydrochloric acid gas.

4. Hydrogen chloride is also formed when a mixture of steam and chlorine is passed through a red-hot porcelain tube.



Properties.—Hydrogen chloride is a colourless gas of specific gravity 18·25, and is therefore somewhat heavier than air; it possesses a pungent odour, and an intensely acid taste; it is neither combustible nor a supporter of combustion. It fumes when brought into contact with the air, owing to its dissolving in the moisture of the air, and forming a cloud of hydrochloric acid. It is very soluble in water, 1 volume of water dissolving 454 volumes of the gas at ordinary temperatures; this solution of the gas in water constitutes strong *hydrochloric* or *muriatic acid*. It is a fuming liquid of specific gravity 1·16, and containing 32 per cent. by weight of hydrogen chloride. The acid of constant composition has a specific gravity 1·1, contains 20·2 per cent. of HCl, and boils at 110°. All other mixtures of acid and water, on being boiled, rise or fall in strength till this constant composition is attained, the superfluous acid or water being boiled away. The strong acid is decomposed by a current of electricity (using gas-carbon electrodes) into its elements, equal volumes of chlorine and hydrogen being liberated, the former at the anode and the latter at the kathode (at first only hydrogen is evolved, all the chlorine being dissolved in the fluid).

Hydrochloric acid is very useful in the laboratory as a solvent; it dissolves many metals (page 74) forming chlorides: all chlorides are soluble in water,

except silver, mercurous, cuprous, and lead chlorides (the latter dissolves in hot water).

Tests.—1. *For the gas.* It fumes when brought into contact with the air, and also produces a dense white cloud when brought into contact with ammonia gas; it turns moist blue litmus paper red.

2. *For the liquid.*—Nitrate of silver gives a white curdy precipitate, which is insoluble in strong nitric acid, but is soluble in solution of ammonia.

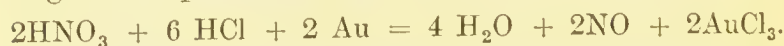
3. When hydrochloric acid is heated with MnO_2 , chlorine gas is evolved, and can easily be identified by the tests described for that element (page 175).

NITRO-HYDROCHLORIC ACID, OR AQUA REGIA

These names are given to a mixture of strong nitric and hydrochloric acids; the mixture has a very powerful solvent action on metals. Its solvent action on metals is due to the presence of free chlorine, liberated from the hydrochloric acid by the oxidising action of the nitric acid.

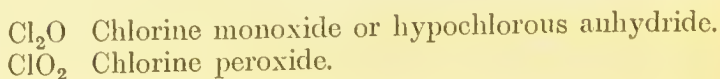


The chlorine unites with the metal forming its *ic* chloride. In the case of gold the complete reaction might be represented thus:



COMPOUNDS OF CHLORINE WITH OXYGEN

Chlorine and oxygen do not unite directly; but indirectly they may be made to form the two following oxides of chlorine:



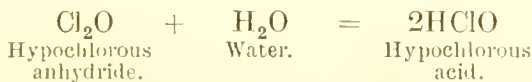
CHLORINE MONOXIDE OR HYPOCHLOROUS ANHYDRIDE

Formula, Cl₂O ; molecular weight, 87.

Mode of preparation.—By the action of dry chlorine gas on *dry* yellow or precipitated mercuric oxide.



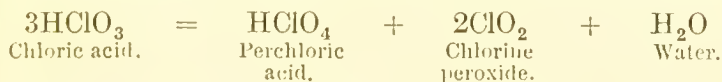
Properties.—Chlorine monoxide is a yellowish gas possessing an odour similar to that of chlorine ; when heated it decomposes into its elements with explosive violence. It unites with water, forming hypochlorous acid.



CHLORINE PEROXIDE

Formula, ClO₂ ; molecular weight, 67.5.

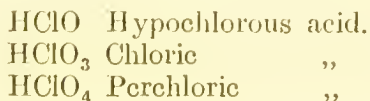
Mode of preparation.—By very gently heating potassium chlorate with pure sulphuric acid, chloric acid is first formed and then breaks up.



Properties.—Chlorine peroxide is a dark yellow gas, exploding with terrific violence when heated. Great care is required in its preparation.

OXYACIDS OF CHLORINE

There are three oxyacids of chlorine, viz. :



The constitution of these acids was fully considered on page 64, to which the student should now refer.

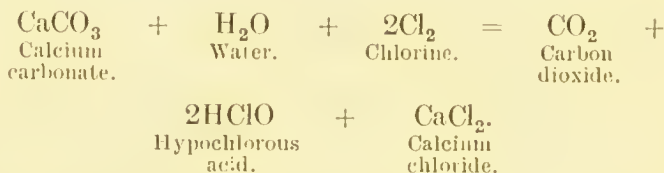
HYPOCHLOROUS ACID

Formula, HClO.

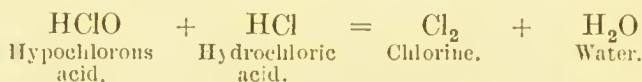
Mode of preparation.—1. By the action of hypochlorous anhydride on water.



2. By shaking chlorine water with calcium carbonate.



Properties and compounds.—Hypochlorous acid, when mixed with hydrochloric acid, suffers decomposition, chlorine being evolved.



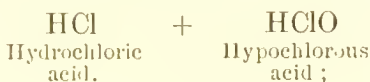
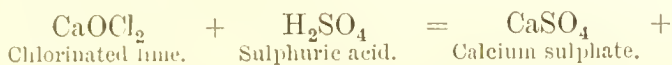
Hypochlorous acid enters into the composition of the **chlorinated bodies**, which readily give rise to a mixture of a chloride and a hypochlorite. The most familiar example of this class is the “chlorinated lime” of the Pharmacopœia, commercially known as “bleaching powder.”

Chlorinated lime.—This is prepared by passing chlorine over damp slaked lime.

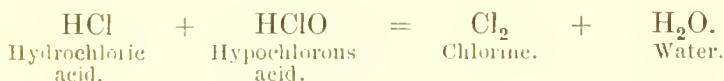


Properties.—Chlorinated lime constitutes *bleaching powder*, or the disinfectant known as *chloride of*

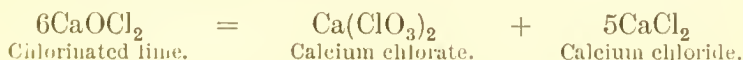
lime. When treated with an acid, such as sulphuric acid, hydrochloric and hypochlorous acids are first set free, and then immediately react on one another, producing free chlorine.



then



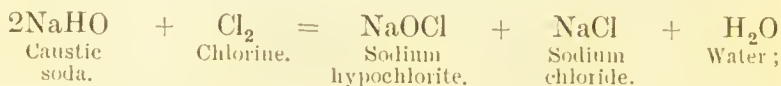
Chlorinated lime is acted on by the weakest acids, for even when exposed to the air, the carbon dioxide (carbonic acid gas) of the air sets free hypochlorous acid, which then decomposes with evolution of chlorine ; it is in this way that *chloride of lime* acts as a disinfectant. Its bleaching powers also depend on the evolution of chlorine. If a solution of chlorinated lime be boiled, it yields chlorate and chloride of calcium.



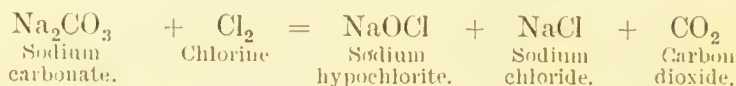
Solid bleaching powder is probably a special *compound* of calcium, chlorine, and oxygen, having the formula $\left\{ \text{Ca} \begin{smallmatrix} \text{Cl} \\ \text{OCl} \end{smallmatrix} \right.$; for, if it were a *mixture* containing calcium chloride, it should be deliquescent, and alcohol ought to dissolve out calcium chloride. Good bleaching powder is not deliquescent, and no CaCl_2 is extracted by alcohol. Moreover, if dry bleaching powder be warmed to 70° and carbon dioxide be passed over it, all the chlorine is evolved, and it is improbable that a chloride should be thus decomposed. When bleaching powder is dissolved in water it seems to break up into a mixture of cal-

cium chloride and calcium hypochlorite. The above formula (CaOCl_2) was first proposed by Odling.

Sodium hypochlorite.—This salt is formed together with the chloride when chlorine is passed into a cold aqueous solution of caustic soda or of sodium carbonate.



or



Properties.—The properties of sodium hypochlorite in solution are similar to those of chlorinated lime. Dilute acids liberate chlorine; boiling its solution converts it into chlorate and chloride of sodium, thus :

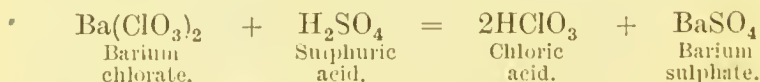


The preparation and properties of the potassium salt are quite similar to those of sodium hypochlorite.

CHLORIC ACID

Formula, HClO_3 .

Mode of preparation.—Chloric acid is most readily prepared by cautiously adding sulphuric acid to a solution of barium chlorate, allowing the precipitated barium sulphate to subside, and then pouring off the clear liquid.



Properties.—Chloric acid is a most powerful oxidising agent. Its salts are the chlorates, of which the most important is potassium chlorate. No

chlorates exist in nature; they therefore have to be made artificially, and, as previously mentioned, they are readily obtained by boiling solutions of the hypochlorites or by passing chlorine into a hot strong solution of caustic alkali. The chlorates are therefore more stable salts than the hypochlorites.

Potassium chlorate (KClO_3).—Prepared by passing chlorine into a heated solution of caustic potash.



On concentrating the solution by evaporation, and then allowing it to cool, the potassium chlorate crystallises out, leaving the more soluble potassium chloride in solution.

Test.—1. When a chlorate is gently heated with strong sulphuric acid a yellow gas, peroxide of chlorine, is evolved, which detonates when heated (*see* page 179).

2. When heated alone, chlorates evolve oxygen and are converted into chlorides. The oxygen may be identified by test (page 109); the residual chloride may be dissolved in water and identified by the tests (page 179).

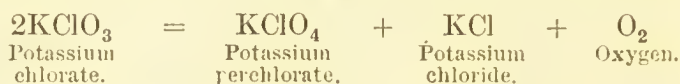
3. Chlorates dissolve in water, and the aqueous solution, when warmed with hydrochloric acid, acquires a yellow tinge, evolves a chlorous smell, and discharges the colour of a solution of indigo sulphate.

PERCHLORIC ACID

Formula, HClO_4 .

Mode of preparation.—In describing the preparation of oxygen from potassium chlorate it was stated (page 101) that the reaction really took place in two stages. If potassium chlorate be strongly

heated it evolves all its oxygen, leaving potassium chloride; but if the salt be heated until it just melts, and then kept for a short time at that temperature, only one-third of the oxygen is evolved, and a mixture of potassium *perchlorate* and chloride is left.



From this mixture the potassium chloride can be extracted by virtue of its greater solubility in water, and the perchlorate obtained pure.

By heating potassium perchlorate with sulphuric acid, perchloric acid distils over.



Properties.—Perchloric acid is a colourless fuming liquid, and is a very powerful oxidising agent. The perchlorates do not evolve an explosive gas when heated with strong sulphuric acid. They are more stable than the chlorates.

CHAPTER VIII

HALOGEN ELEMENTS (*concluded*)

BROMINE: Preparation and Properties of Bromine—Tests for Bromine—Hydrobromic Acid—Hypobromous Acid—Sodium Hypobromite. IODINE: Preparation and Properties of Iodine—Tests for Iodine—Hydriodic Acid—Iodic Acid—Chlorides of Iodine—Iodide of Nitrogen. FLUORINE: Hydrofluoric Acid.

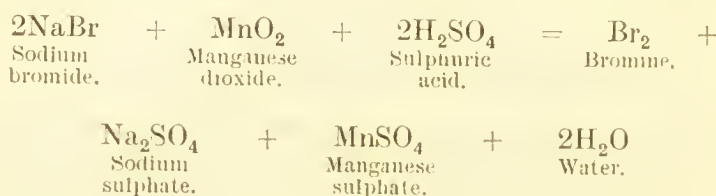
II. BROMINE

Symbol, Br ; *molecule*, Br₂ ; *valency*, as chlorine (page 170) ; *atomic weight*, 80 ; *molecular weight*, 160. *Boils at* 59° ; *freezes at* -7° ; *sp. gr.* 3.188.

BROMINE does not occur in nature in the free state, but in the form of metallic bromides. The bromides of sodium and magnesium are present in small quantities in many mineral springs, and in sea-water ; bromide of potassium is also present in the Stassfurt salts, which occur as deposits on a large scale in Northern Germany.

Mode of preparation.—Bromine may be prepared from the mother liquors of mineral spring waters, or from *bittern*, the mother liquor of concentrated sea-water (from which most of the chlorides have crystallised out), or from Stassfurt salts. The bromine is set free by distilling the mother liquors or the Stassfurt salts with sulphuric acid and manganese dioxide, using only sufficient of these two bodies to liberate the bromine, otherwise the chlorine would also be liberated from the chlorides that are

always present, and would contaminate the bromine by forming with it a chloride of bromine. The liberation of bromine, by the manganese dioxide and sulphuric acid, takes place in a manner similar to the liberation of chlorine by the same reagents.



The bromine passes over as a heavy reddish-brown vapour, which is condensed to a liquid by means of a suitable condenser and cool receiver. The bromine so obtained generally contains small quantities of chlorine, present as chloride of bromine, or as a mere mixture* of chlorine in bromine, from which it can be purified by redistilling with some potassium bromide, thus :



Properties.—Bromine is a heavy liquid (bromine and mercury are the only elements liquid at ordinary temperatures) of a dark red-brown colour, and of specific gravity 3.18 at 0°. It is very volatile, forming a reddish-brown vapour possessing a disagreeable odour, somewhat resembling that of chlorine but much more intense. This vapour is poisonous and is extremely irritating to the mucous membranes of the eye, nose, and respiratory passages; the name of the element is derived from *βρῶμος*, a *stink*, on account of its extremely disagreeable smell. It is soluble to a certain extent in water, bromine-water being of a reddish-brown colour. Its

* See Chemical Society's Annual Reports, vol. iv., p. 67.

chemical affinities for hydrogen and the metals are weaker than those of chlorine, which can be demonstrated by adding a few drops of chlorine-water to a solution of potassium bromide, when the development of a reddish-brown colour in the solution indicates the liberation of the bromine, thus :



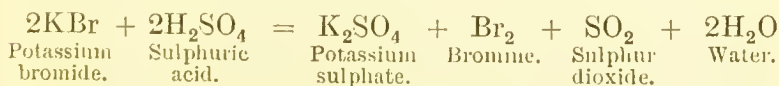
Tests.—In the pure state, bromine is readily recognised by its colour and smell ; in the diluted state, such as in weak bromine-water, it may be recognised (*a*) by its colour becoming intensified by the addition of some decoction of starch ; (*b*) by giving a white precipitate on the addition of an aqueous solution of carbolic acid ; (*c*) by shaking with a drop of chloroform or carbon bisulphide, which dissolves out the bromine and becomes coloured brown.

HYDROGEN BROMIDE

Formula, HBr ; molecular weight, 81.

Hydrogen bromide, like hydrogen chloride, is a colourless gas, fuming when brought into contact with the air, and very soluble in water, its solution forming the commercial hydrobromic acid.

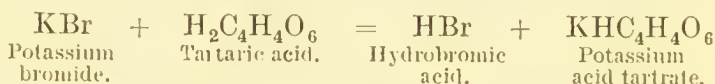
Modes of preparation.—Hydrogen bromide cannot be prepared by the action of strong sulphuric acid on a bromide, because the acid decomposes the hydrogen bromide, so that free bromine is liberated.



It can, however, be prepared (1) by the action of bromine on phosphorus in the presence of water.

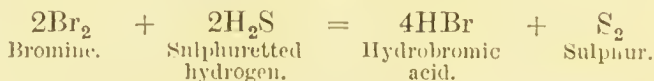


2. By shaking together strong solutions of potassium bromide and tartaric acid, and allowing the mixture to stand for some time to enable the precipitated acid tartrate of potassium to subside; the clear solution of hydrogen bromide can then be poured off from the precipitate.



3. By distilling potassium bromide with phosphoric acid, when phosphate of potassium is formed, and hydrobromic acid passes over.

4. By passing sulphuretted hydrogen through bromine-water, when a solution of hydrogen bromide is formed and sulphur precipitated.



5. By direct union of hydrogen and bromine in presence of heat.



Tests.—1. On the addition of a few drops of chlorine-water to a solution of hydrobromic acid or a bromide, bromine is liberated, a yellowish-red colour being communicated to the solution; on shaking with a drop of chloroform or carbon disulphide the bromine is dissolved and colours the drop brown.

2. On the addition of nitrate of silver to a solution of hydrobromic acid or a bromide, a whitish precipitate is formed, insoluble in nitric acid, and but sparingly soluble in ammonia.

Potassium bromide deserves special mention, as it is frequently prescribed. An account of the preparation and properties of this compound will be found in the chapter on potassium (page 269).

OXYACIDS OF BROMINE

There are two of these acids, viz. :

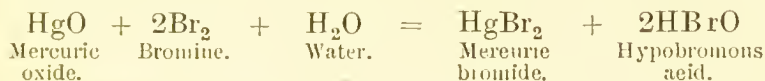
HBrO Hypobromous acid.

HBrO₃ Bromic „

HYPOBROMOUS ACID

Formula, HBrO.

Prepared by shaking bromine-water with the yellow precipitated mercuric oxide.



Sodium hypobromite is formed when bromine is shaken with a cold solution of sodium hydroxide, $\text{Br}_2 + 2\text{NaOH} = \text{NaBr} + \text{NaOBr} + \text{H}_2\text{O}$. It is employed in the estimation of urea in urine. It decomposes the urea, oxidising the carbon and hydrogen to carbon dioxide and water, and setting free the nitrogen, thus :



The nitrogen can then be collected and measured (the process is described fully in Organic Chemistry, Chapter IX.).

III. IODINE

Symbol, I; *molecule*, I₂*; *valency*, as chlorine (page 170); *atomic weight*, 127; *molecular weight*, 254; *melts at* 114°; *boils at* 184°; *sp. gr.*, 4.94.

Iodine does not occur in nature in the free state. The iodides of sodium and magnesium are present in

* But see page 45.

small quantities in certain mineral spring waters, and in still smaller quantities in sea-water. Large quantities of iodine are now obtained from the deposits of "nitrates" in Chili, where it occurs as sodium iodate. The amount of iodides (mainly sodium iodide) present in sea-water is so minute as to make it impracticable to extract the iodine from sea-water, but sea-weeds possess the property of absorbing the iodides into their tissues in considerable quantities, and it is from sea-weeds that iodine is extracted. The sea-weeds (Scottish and Irish sea-weeds being especially rich in iodine) are collected, dried, and burnt, when an ash named *kelp* is obtained, and it is from this kelp that iodine is prepared. The bulk of the kelp, or sea-weed ash, consists of sodium carbonate, together with sodium chloride, sodium sulphate and sodium sulphide, and small quantities of sodium and magnesium iodides.

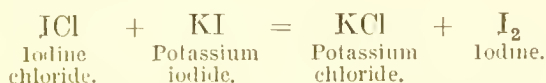
Mode of preparation of iodine from kelp.

—The kelp is treated with boiling water, and the solution poured off from the insoluble matter; to the solution sulphuric acid is added, when carbon dioxide and sulphuretted hydrogen gases are evolved, sulphur is thrown down, and after standing for twenty-four hours a large quantity of sodium sulphate crystallises out; the mother liquor from the sodium sulphate crystals is then poured off, and contains in solution the iodides with some sodium chloride and free sulphuric acid; to it manganese dioxide is added, and the mixture distilled at a temperature not exceeding 80° , at which temperature the man-

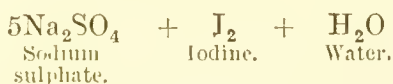
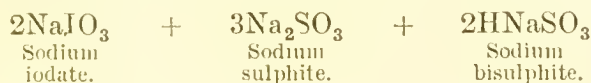


ganese dioxide and sulphuric acid liberate the iodine, but not the chlorine, or only in very small quantities. (For equation, *see* page 190.)

The iodine passes over in the form of a violet-coloured vapour, which is made to pass through a series of cooled glass condensers, on the sides of which it condenses as a dark-coloured solid. The iodine so prepared generally contains a small quantity of chlorine in the form of a chloride of iodine, from which it can be purified by resubliming it from some potassium iodide.



Preparation from Chili saltpetre.—After the bulk of the sodium nitrate has crystallised out, the mother liquor contains about 22 per cent. of sodium iodate; it is treated with a mixture of sodium sulphite and bisulphite, when the iodine is precipitated, is ladled out, squeezed, and sublimed.



Properties.—Iodine is a solid crystalline substance, possessing a dark grey colour, a metallic lustre, and a peculiar odour somewhat resembling that of diluted chlorine. When heated it volatilises, producing a violet-coloured vapour (hence its name, from *ιώδης*, *violet-coloured*), which is very irritating to the mucous membrane of the eyes and nose. Iodine possesses a strong unpleasant taste, it stains the skin yellow, and is poisonous. It is slightly soluble in water, to which it imparts a yellowish-brown colour; it is much more soluble in a solution

of iodide of potassium, in alcohol, ether, chloroform, or bisulphide of carbon. The tincture of iodine of the B.P. is an alcoholic solution of iodine and potassium iodide.

Tests.—1. A solution of free iodine gives with a cold decoction of starch a deep blue colour.

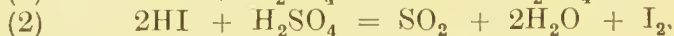
2. If with an aqueous solution of iodine some chloroform or bisulphide of carbon be well agitated, and the mixture allowed to stand, the chloroform or bisulphide of carbon will settle to the bottom of the tube, carrying the iodine in solution, a pink or purple colour being imparted to the chloroform or bisulphide of carbon by the dissolved iodine.

HYDROGEN IODIDE

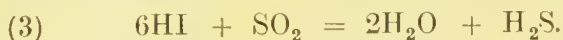
Formula, HI ; molecular weight, 128.

Hydrogen iodide, like hydrogen chloride and hydrogen bromide, is a colourless gas, fuming when brought into contact with the air, and very soluble in water, its solution forming the ordinary hydriodic acid.

Hydrogen iodide can be prepared by union of its elements, but only with great difficulty. By distilling potassium iodide with strong sulphuric acid, hydrogen iodide is formed, but is immediately decomposed by the acid, iodine being set free, while the sulphuric acid is reduced to sulphur dioxide, thus :



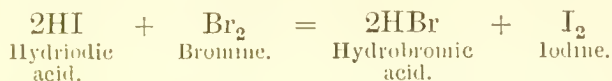
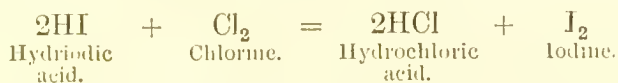
and the reduction may even go so far as to produce sulphuretted hydrogen, thus :



Modes of preparation.—These are exactly analogous to the methods used to prepare hydrogen bromide.

The equations on pages 187-88 will represent the reactions, if iodine be substituted for bromine.

Properties.—Both chlorine and bromine have stronger affinities for hydrogen and for the metals than iodine, therefore both chlorine and bromine possess the property of liberating iodine from hydriodic acid or from an iodide, thus :



Hydriodic acid on exposure to light becomes coloured from liberation of iodine. An aqueous solution of potassium iodide slowly suffers the same change. Potassium iodide is a valuable drug. It is described later (page 268).

Tests.—1. On the addition of a few drops of chlorine-water to a solution of hydriodic acid or of an iodide, a yellowish-brown colour is produced, due to the liberation of iodine; if some solution of starch be added to this, a deep blue colour will be produced.

2. On the addition of nitrate of silver to a solution of hydriodic acid or of an iodide, a yellowish precipitate is formed, insoluble in nitric acid, and almost insoluble in ammonia.

IODIC ACID.

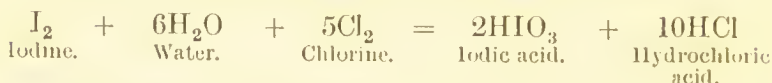
Formula, HIO₃.

Iodic acid is a white crystalline substance, and is prepared

1. By the action of strong nitric acid on iodine



2. By passing chlorine into iodine-water.



Potassium iodate is obtained in the preparation of potassium iodide (page 268), and could be separated if required. It can also be obtained by heating iodine with potassium chlorate.



Iodine therefore displaces chlorine from its oxy-compounds, but chlorine displaces iodine from metallic compounds.

CHLORIDES OF IODINE

There are two compounds of iodine and chlorine, viz. ICl , a liquid, and ICl_3 , a solid. They are both obtained by direct union of the elements. ICl_3 is believed to decompose readily into the more stable ICl and Cl_2 , and in this way to act as a carrier of chlorine.

IODIDE OF NITROGEN

This is obtained by mixing a strong alcoholic solution of iodine (such as tincture of iodine) with an aqueous solution of ammonia. Various formulæ have been assigned to this substance, NI_3 , NH_3I_2 , etc.; the latest is $\text{N}_2\text{H}_3\text{I}_3$.

Properties.—Iodide of nitrogen is a dark-coloured powder, which, when dried, explodes violently with the slightest touch, decomposing into its elements. The importance to medical men of bearing in mind its existence lies in the fact that free iodine and ammonia are incompatibles, and should not therefore be prescribed together in a liniment.

IV. FLUORINE

Symbol, F ; molecule, F₂ ; monad (in fluorides) ; atomic weight, 19 ; molecular weight, 38.

Fluorine occurs in nature as *fluor-spar* or calcium fluoride (CaF₂), and as *cryolite*, a double fluoride of aluminium and sodium (AlF₃, 3NaF) found in Greenland. The fluorides of calcium and sodium are also present in minute quantities in the blood, bones, and teeth of human beings and animals.

Fluorine was first satisfactorily isolated by Moissan in 1886. This chemist obtained it by the electrolysis of a solution of potassium fluoride in hydrofluoric acid, using a platinum U-tube, and keeping the solution at a temperature of -23° . It is a pale yellowish-green gas, liquefied by Dewar and Moissan at a temperature of -187° , and frozen, by means of liquid hydrogen, at -223° . Both liquid and solid have a yellow colour, but the solid is quite white at -252° . Fluorine combines, usually with great violence, with all elements except oxygen, nitrogen, and chlorine.

HYDROGEN FLUORIDE

Formula, HF.

Like the corresponding compounds with chlorine, bromine, and iodine, hydrogen fluoride is a colourless gas, fuming on contact with the air, and very soluble in water, its solution constituting the commercial hydrofluoric or fluoric acid.

Mode of preparation.—Hydrogen fluoride is obtained by the action of strong sulphuric acid on powdered fluor-spar, thus :



It has to be prepared in leaden or platinum vessels, as it readily attacks glass; on conducting the gas into water, the commercial solution of hydrofluoric acid is obtained.

Properties.—The most important property of this acid is its power of etching glass, which is due to its attacking the silica of glass, forming with it a gaseous silicon fluoride, thus :



If a design is to be etched on glass, the surface of the glass is first covered with wax, the design is then scratched through the wax, and the surface exposed for a few minutes to the fumes of hydrofluoric acid (evolved from fluor-spar and sulphuric acid), or the solution of hydrofluoric acid is poured over the surface; on washing the surface with a stream of water, and then scraping or melting off the wax, the design will be found to be etched on the glass. On account of its power of attacking glass, the solution of hydrofluoric acid is kept in bottles made of gutta-percha, provided with a stopper of the same material. It is possibly a dibasic acid with the formula H_2F_2 .

Test.—The test for hydrofluoric acid is to expose to it a piece of waxed glass, on which some simple design has been scratched, when the design will in a short time be etched on the glass.

CHAPTER IX

CARBON—SILICON—BORON

CARBON: Allotropic Forms of Carbon—Carbon Monoxide—Carbon Dioxide—Carbonates—Carbon Oxychloride—Carbon Bisulphide—Coal Gas—Combustion—Nature of Flame. SILICON: Silica, Silicates, Glass, Porcelain, and Earthenware. BORON: Boric Acid—Metaboric Acid—Borax.

CARBON

Symbol, C; tetrad; atomic weight, 12.

CARBON occurs in nature in the free state in the diamond, graphite, plumbago, coal, etc. In the combined state it enters into the composition of an immense number of bodies, for the number of carbon compounds (both natural and artificial) far exceeds those of any other element; it occurs in all organic substances, whether of animal or of vegetable origin, and in all carbonates, such as marble, limestone, chalk, magnesite, etc.

Carbon exists in three allotropic (page 114) forms, of which two are crystalline—viz. *diamond* and *graphite*, and one amorphous—viz. *charcoal* in its different forms.

The allotropic forms of carbon. 1. *Diamond*.—*Sp. gr.*, 3.5. This is the rarest form of free carbon, and occurs in nature in octahedral crystals belonging to the regular system; it consists of nearly pure carbon, but when a diamond is burnt in oxygen a minute amount of ash is left, consisting

of silica, alumina, and sometimes oxide of iron. It is the hardest body known, and is employed for cutting glass; the property of *cutting* glass depends on the *curved* edge which many diamond crystals possess. Its lustre is due to its high power of refracting light. Moissan has prepared microscopic crystals of diamond by dissolving carbon in melted iron and cooling the whole suddenly. The iron is dissolved by acids, and in the residue some minute diamond crystals are found.

2. *Graphite, plumbago, or blacklead*.—*Sp. gr.* 2·2. This is the second crystalline form of carbon, and crystallises in six-sided plates. It is a dark-grey crystalline substance, soft and greasy to the touch, and when drawn across paper leaves a mark. It is employed in blacklead pencils, in plumbago crucibles (made of plumbago mixed with clay), for blacking iron grates, and as a dry lubricant for machinery.

3. *Amorphous carbon: Charcoal*.—*Sp. gr.*, 1·5. Various forms are recognised.

(1) *Wood charcoal* is prepared by heating or charring wood out of contact with air. This form of amorphous carbon is used in the manufacture of gunpowder. It is extremely porous, possessing the power of absorbing gases, and hence is used as a deodoriser.

(2) *Animal charcoal* is obtained by heating bones out of contact with air. This form of amorphous carbon is sold commercially under the names of *bone-black*, *animal-black*, and *ivory-black*; it contains the inorganic constituents of the bones—viz. phosphate and carbonate of lime, from which, however, it may be freed by digesting with hydrochloric acid, which dissolves these lime salts, so that on filtering, and washing the charcoal with water, it is obtained pure. Animal charcoal possesses in a very high degree the power of absorbing colouring matters, and hence is

very useful as a decolorising agent. In the preparation of several of the alkaloids, the colouring matter is removed by boiling the alkaloidal solution with animal charcoal. In the manufacture of sugar, the crude brown syrup is filtered hot through animal charcoal to decolorise it.

(3) Amorphous carbon is the chief constituent of *coal*. Coal has been produced by the slow decay of vegetable matter out of contact with air, possibly combined with elevation of temperature and considerable pressure.

(4) *Peat*, another form of fuel, but inferior to coal, contains a quantity of amorphous carbon; it is produced in marshy localities by the gradual decay of grasses, mosses, etc.

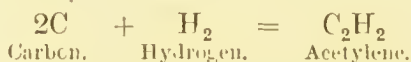
(5) *Tinder* is a variety of amorphous carbon.

(6) *Soot* and *lampblack* are two varieties of amorphous carbon in a fine state of division.

Properties of carbon.—In all three of its forms carbon is infusible at all temperatures, but it volatilises at the high temperature of the electric arc. It is insoluble in all ordinary solvents, but molten iron at the temperature of the blast-furnace dissolves from 4 to 5 per cent. of carbon; as the iron cools, part of the carbon crystallises out as small crystals of graphite, and part remains in union with the iron as carbide of iron (page 362). Carbon when heated to redness has a powerful affinity for oxygen, either in the free state as in air, or in the combined state; it is therefore largely employed as a reducing agent for depriving many of the metallic oxides of their oxygen, and so reducing them to the metallic state. If carbon be burnt in a free supply of air it produces carbon dioxide (CO_2), but if burnt in a limited supply of air it produces mainly carbon monoxide (CO).

Carbon unites with hydrogen to form a large

number of compounds known as *hydrocarbons*. Four of these have already been mentioned (page 41), and others will be described later; one such compound is obtained by direct union of carbon and hydrogen—viz. *acetylene* (C_2H_2), at the temperature of the electric arc; if the electric arc is produced between carbon poles in an atmosphere of hydrogen, then the two elements unite to form acetylene, thus:



Test.—Any form of carbon (including the diamond) when burnt in oxygen produces carbon dioxide, which can be recognised by its turning lime water turbid. Even when carbon is present, not as an element but in combination, its presence may be established by this test. The carbon compound mixed with copper oxide and heated evolves carbon dioxide.

CARBON MONOXIDE

Formula, CO; molecular weight, 28; liquefies -190° ; freezes at -211° ; critical temperature, -139.5° .

Also known as *carbonic oxide*.

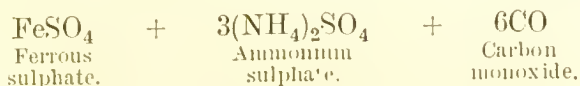
Modes of preparation.—1. By passing carbon dioxide through a tube containing pieces of red-hot charcoal.



The blue flames seen at the top of a well-drawing clear fire consist of burning carbon monoxide, which has been produced by the carbon dioxide, formed at the lower part of the fire, having to pass over the red-hot coal on its upward way to the chimney.

2. Carbon monoxide is very easily prepared by

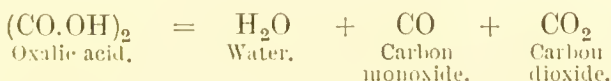
heating potassium ferrocyanide with *strong* sulphuric acid.



3. Carbon monoxide is also readily prepared by heating formic acid (H.CO.OH) or sodium formate (H.CO.ONa) with strong sulphuric acid. The action of the sulphuric acid is simply to abstract water from the formic acid, when carbon monoxide is evolved, thus :



4. If oxalic acid be heated with strong sulphuric acid, it decomposes into water and the two oxides of carbon, thus :



By passing the two gases through a strong solution of caustic potash, the carbon dioxide is absorbed (forming potassium carbonate), and the carbon monoxide can then be collected in the pure state.

5. When charcoal or carbonaceous substances are burnt with an insufficient supply of air, carbon monoxide is formed.

Properties.—The specific gravity of carbon monoxide is 14, and it is slightly lighter than air ; it is a colourless, almost odourless, and tasteless gas ; it is combustible, burning with a pale blue flame, and forming carbon dioxide ; it is a non-supporter of combustion ; it is insoluble in water, and therefore may be collected over it. It is a poisonous gas,

as it possesses the property of displacing the oxygen from its union with the hæmoglobin of the blood, forming a compound with the hæmoglobin which acts as a narcotic poison; inhaling the fumes of burning charcoal, placed in the centre of a closed and non-ventilated room (a not uncommon method of committing suicide in France), causes death from carbonic oxide poisoning. An atmosphere containing 0.2 per cent. renders a man helpless and unconscious in about half an hour. A small animal such as a mouse succumbs in about one-twentieth of the time. Carbon monoxide in contact with caustic potash at a high temperature produces potassium formate, thus:



This reaction suggests that carbon monoxide is really *formic anhydride*. Carbon monoxide, when passed over finely divided nickel or iron gently heated, combines with these metals to form vapours which condense to liquids; nickel carbonyl, which is colourless, has the formula Ni(CO)_4 . If the vapour of nickel carbonyl be passed through a glass tube heated to 200° , it is decomposed, and the nickel is deposited on the glass as a bright mirror-like coating.

Test.—Carbon monoxide gives no precipitate with lime-water, but on applying a light it burns with a pale blue flame, and the resulting gas (carbon dioxide) then produces a precipitate with lime-water.

CARBON DIOXIDE

Formula, CO_2 ; molecular weight, 44; liquefies -78° ; critical temperature, 31° .

Also known as *carbonic anhydride*, *carbonic acid gas*, and *choke-damp*. It is always formed when carbon in any form, or any compound of carbon, is

burnt with a free supply of air. It is one of the gases evolved from volcanoes, and in certain instances from fissures in the earth, as in the Grotto del Cane near Naples, and in the poison valley of Java.

Modes of preparation.—1. All carbonates, when acted on by any of the common reagent acids, evolve carbon dioxide, usually with marked effervescence, and are thus identified. The gas is, in fact,

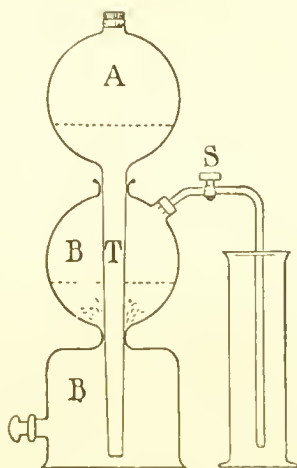


Fig. 25.—Kipp's apparatus for the supply of carbon dioxide, sulphuretted hydrogen, etc. (*see text*).

most commonly prepared by the action of hydrochloric acid on calcium carbonate in the form of marble or chalk.



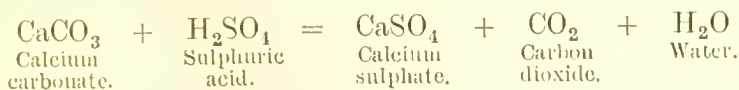
It is heavier than air, and can be conveniently collected by downward displacement of air.

Kipp's apparatus, shown in Fig. 25, is often employed for obtaining a fairly regular supply of the gas when required. It consists of a glass bulb A drawn out below into a long tube T, and a

double glass vessel B B constricted at the middle. T is ground to fit closely into the *upper* opening of B, but fits more loosely at the constriction, where a rough glass collar is often placed also, so that liquids can pass to and fro between the two compartments of B, but solids of appreciable size would be prevented from doing so. For the present purpose, lumps of marble are placed in the upper chamber of B B; A is then placed in position, the tap s turned "on," and hydrochloric acid poured into A till it fills the lower compartment of B B, and, rising through the constriction, comes into contact with the marble. Carbon dioxide is then evolved, and issues freely through s. When enough gas has been collected, the tap s is turned "off." The gas has now no means of escape, and therefore accumulates in the confined space above the acid in the upper part of B B. It now exerts increased pressure, and forces the acid back into the lower compartment of B B, whence it rises up T into A. The acid having now been removed from the marble, no further action takes place, and the apparatus will remain as it is till again required. When s is again turned "on," the acid will at once descend from A and rise in B B till it again reaches the marble, when action will recommence. In time, the acid becomes exhausted, and can then be drawn off from the lower compartment of B B, and replaced by fresh acid poured down from A as at first. This apparatus can evidently be used for obtaining a supply of any other gas which results from a similar reaction without the application of heat. It is, in fact, very commonly employed in the laboratory to furnish a supply of sulphuretted hydrogen when required for analytical purposes.

If sulphuric acid be substituted for hydrochloric acid in the preparation of carbonic anhydride, the

insoluble calcium sulphate forms a coating over the marble or chalk, and checks the evolution of the gas.



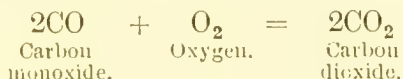
2. Carbon dioxide is evolved by heating chalk or limestone, as in the preparation of lime in the limekilns.



3. Carbon dioxide is also evolved by heating a bicarbonate, such as sodium or potassium bicarbonate. The acid salt is converted into the normal salt at the same time.

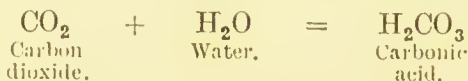


4. By burning carbon monoxide in oxygen or in air, carbon dioxide is produced.



Properties.—The specific gravity of carbon dioxide is 22, and it is heavier than air; it is a colourless gas, possessing a peculiar faint pungent odour in quantity, and a faint acid taste; it is not combustible, neither is it a supporter of combustion, a lighted taper being immediately extinguished when lowered into the gas. It can be liquefied by a pressure of 38·5 atmospheres at 0°, and if the liquid is allowed to escape into the air, the portion that evaporates so lowers the temperature of the remaining portion that it solidifies. It is slightly soluble in water, as at ordinary temperatures water dissolves its own volume of the gas; under a pressure of two atmospheres water will dissolve twice its volume of

the gas, under a pressure of three atmospheres three times its volume, under a pressure of four atmospheres four times its volume, and so on (the volume of the dissolved gas being measured in each case at the same ordinary temperature and pressure). If, therefore, a pint bottle of soda-water that has been charged under a pressure of four atmospheres be opened, three pints of the gas will escape with effervescence, one pint remaining in solution, since there is still the ordinary pressure of the atmosphere upon the water. The solution of carbon dioxide in water faintly reddens blue litmus paper, the liquid probably containing true carbonic acid (H_2CO_3), thus :



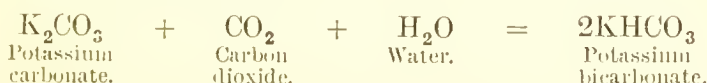
It is for this reason that carbon dioxide is also called carbonic anhydride (the anhydride of carbonic acid) and carbonic acid gas. Carbon dioxide is not a poison if swallowed into the stomach, as in the form of effervescent waters and drinks it is taken in considerable quantities, but if *inhaled* in quantity it produces death from suffocation, not that it unites with the hæmoglobin of the blood, but because it dilutes down and keeps out the necessary oxygen of the air. After explosions in coal-mines, it is the carbon dioxide, mixed with some carbon monoxide (after-damp), produced by the explosion of the marsh-gas, or fire-damp, with the air, that causes in so many cases the suffocation of the miners. Since carbon dioxide is evolved, as previously mentioned, from limekilns, it is not an uncommon occurrence for tramps and others sleeping close to a limekiln, for the sake of the warmth, to die in their sleep, suffocated by this gas. If pure carbon dioxide is inhaled, it produces spasm of the glottis and consequent death from asphyxia, unless the inhalation of the

gas is immediately stopped. Carbon dioxide, as previously explained, is largely used in the so-called aerated waters, to give to them their effervescent character and their pleasant sharp taste.

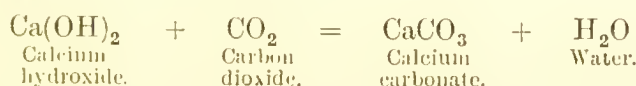
Carbon dioxide, if passed into a solution of an alkali, forms first a carbonate, and then converts the carbonate into a bicarbonate. Thus, with caustic potash it first forms potassium carbonate.



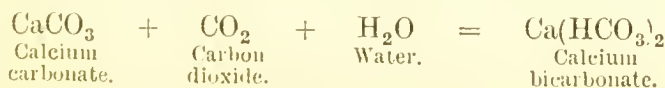
By its further action it converts the carbonate into the bicarbonate.



Carbon dioxide passed into lime-water (solution of calcium hydroxide) first renders it turbid by precipitating calcium carbonate.



By its further action it converts the insoluble calcium carbonate into the soluble bicarbonate, and so renders the liquid clear again. {



Test.—Carbon dioxide turns lime-water turbid or milky when shaken up with it.

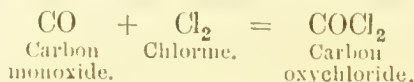
CARBON OXYCHLORIDE

Formula, COCl₂.

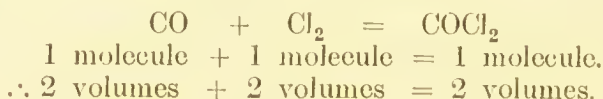
Also known as *carbonyl chloride* and *phosgene gas* (so named on account of its being produced by the

action of light). It is a colourless gas, with marked odour; liquefies at 8° .

Mode of preparation.—It is produced when equal volumes of carbon monoxide and chlorine are exposed to direct sunlight, thus :



When the two gases unite, the volume of the mixed gases diminishes to one-half.



It may also result from the gradual oxidation of chloroform (page 464) exposed to air and light.

By the action of ammonia on this substance urea is formed.



Water decomposes the substance into carbon dioxide and hydrochloric acid :



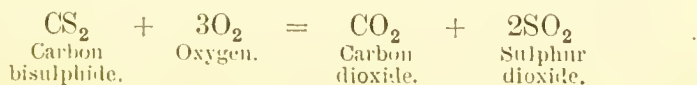
CARBON BISULPHIDE OR DISULPHIDE

Formula, CS₂.

As sulphur and oxygen are analogous elements and appear in the same group in the periodic table (page 88), so this body may be regarded as the sulphur analogue of carbon dioxide. The place of the oxygen has been taken by sulphur, and just as carbon dioxide is produced by burning carbon in oxygen, so carbon bisulphide is produced by burning carbon in sulphur vapour.

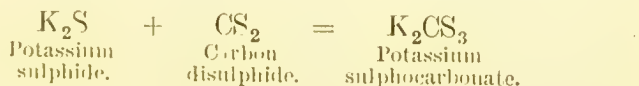
Mode of preparation.—By passing the vapour of sulphur over red-hot charcoal, and then conveying the vapour of the bisulphide of carbon through a spiral tube kept cool by immersion in water, by which means the bisulphide of carbon condenses to a liquid.

Properties.—Bisulphide of carbon is a colourless, mobile, very volatile liquid. When first prepared it possesses a very disagreeable odour, from which it can, to a great extent, be purified by shaking with mercury and corrosive sublimate, and redistilling. It is heavier than water, and after agitation with water it sinks to the bottom, leaving a very small quantity dissolved in the water. It is a very inflammable liquid, boils at 46° , and the vapour takes fire at 149° , so that it can be lighted by a tube of hot paraffin wax. It freezes at -116° . It forms carbon dioxide and sulphur dioxide when burnt.



Carbon bisulphide is used for many technical purposes, as it is an excellent solvent of many bodies, possessing the property of dissolving sulphur, phosphorus, fats, resins, and india-rubber.

With certain of the metallic sulphides carbon disulphide will unite, forming sulphocarbonates, which may be regarded as carbonates in which the oxygen has been displaced by sulphur; thus with potassium sulphide it forms potassium sulphocarbonate.



COAL GAS

Coal gas is a mixture of gases, consisting mainly of hydrogen and hydrocarbons, produced by the dry

or destructive distillation of coal. The coal is heated, without contact of air, in iron retorts, and the products of its destructive distillation are made, first, to pass through condensers in which, as a result of the cooling they are subjected to, the heavy coal-tar and the lighter ammoniacal gas-liquor are condensed and collected in tanks; secondly, the gas is led through towers filled with wet coke to dissolve out the ammonia, and then through purifying chambers, containing either moist slaked lime or ferric oxyhydrate spread on shelves, either of which removes the gaseous impurities containing sulphur, the former removing carbon dioxide as well; finally, the gas is stored in a gasometer. Modern coal gas contains some quantity of "water gas"—i.e. the mixture of carbon monoxide and hydrogen obtained by passing steam over red-hot coke.

The constituents of coal gas may be divided into three groups—*diluents*, *illuminants*, and *impurities*. The *diluents* are gases which, without conferring much luminosity on coal gas when burnt, yet serve the important purpose of diluting down the heavy hydrocarbons, which by themselves would yield a smoky flame; they constitute about 90 per cent. by volume of the coal gas. The *illuminants* are hydrocarbon gases or vapours rich in carbon, and to their presence the luminosity of coal gas when burnt is due; they constitute about 5 per cent. by volume of the coal gas. The *impurities* consist of nitrogen derived from a little air getting into the retorts when opened for the purpose of recharging, and of some carbon dioxide, ammonia, and traces of sulphur compounds which may have escaped removal in the purifiers. Coal gas is therefore a *mixture* (page 7), and the composition of different samples will vary within certain limits. The following is fairly representative:—

COMPOSITION OF COAL GAS.

		By volume.
Diluents	{ Hydrogen	{ 52 per cent.
	{ Methane or marsh gas	{ 34 „ „
	{ Carbonic oxide	{ 6 „ „
Illuminants	{ Ethylene or olefant gas	{ 4 „ „
	{ Acetylene	{ 4 „ „
	{ Benzene vapour	{ 4 „ „
Impurities	{ Nitrogen	{ 4 „ „
	{ Ammonia	{ 4 „ „
	{ Carbon disulphide vapour,	{ 4 „ „
	{ etc.	{ 4 „ „
	{ Carbon dioxide	{ 4 „ „

COMBUSTION

It was explained (page 94) that all common instances of combustion are really examples of oxidation, attended by the evolution of heat and light, and that the terms “combustible” and “supporter of combustion” are merely relative. The following experiment proves this to be the case with coal gas and air. The glass lamp chimney L is fitted with two corks, through which pass the three glass tubes A, B, and c (Fig. 26). B is connected by rubber tubing to the ordinary gas supply. By turning on the gas and closing c with the finger, L is filled with coal gas, which presently issues from A. On applying a light to A, and removing the finger from c, the burning gas is drawn up A, and the air follows it and burns in the atmosphere of coal gas

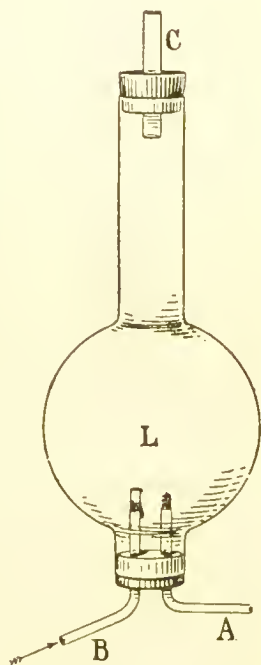


Fig. 26.—Apparatus to show the simultaneous combustion of coal gas in air and air in coal gas (see text).

in L with a faintly luminous flame. At the same time the coal gas issuing from c may be lighted, and be seen burning in air. If a spiral of platinum wire be fused to the inner end of A, it will be rendered red-hot by the flame of burning air, the presence of which is thus more clearly shown.

STRUCTURE OF GAS OR CANDLE FLAME

A gas or candle flame consists of three layers (Fig. 27)—an outer or colourless layer A, consisting of completely burnt gases; a middle or luminous layer B, consisting of partially burnt gases, and containing floating in it minute particles of carbon; and an inner or colourless layer c, consisting of unburnt gases.

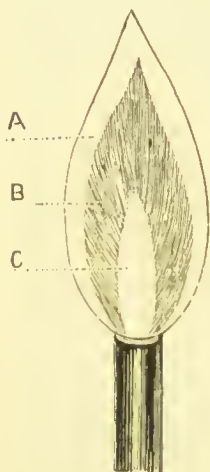


Fig. 27. - Structure of gas or candle flame.

Taking the gas flame by way of illustration, in the outer layer A, both the hydrogen and the carbon of the gaseous constituents are completely oxidised by the oxygen of the air to water and carbon dioxide; to the middle layer B only a limited supply of oxygen from the air can gain access, most of it being used up in the outer layer; the hydrocarbons are therefore only partially burnt, and some particles of carbon (or dense hydrocarbon vapours) which are set free are rendered incandescent by the heat of the flame, and so emit the white light to which the luminosity of the flame is due. The presence of free carbon in the middle layer can be demonstrated by inserting a piece of white porcelain into the flame, when the carbon is deposited on it as soot or lamp-black. The inner layer of the flame must necessarily consist of unburnt gas, since as there is insufficient oxygen

reaching the middle layer for the complete combustion of its constituents, none can gain access to the inner layer. If air is introduced with the gas from within the flame, as in the Bunsen burner, then complete combustion of both the hydrogen and the carbon of the gas occurs, and the result is the colourless Bunsen flame.

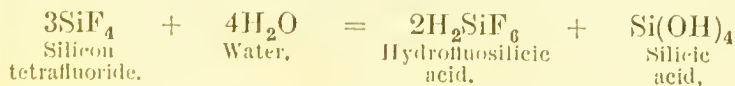
The temperature of a gas flame is very high in an ordinary flat flame burner, about 1370° ; a Bunsen flame is about 1500° . According to some observers, the luminosity of a gas flame is caused by the decomposition of the ethylene into marsh gas and carbon when the particles of the latter become incandescent. The enormous economy in the consumption of gas effected by the Welsbach incandescent burner is due to the fact that the 86 per cent. of hydrogen and marsh gas, which in an ordinary burner produces practically no light, is utilised in the incandescent burner to heat, and thus render luminous, the infusible mantle.

SILICON

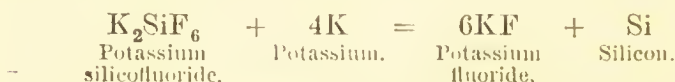
Symbol, Si; tetrad; atomic weight, 28.

Silicon is widely and abundantly distributed in nature, but not in the free state. Next to oxygen it is the chief constituent of the earth's crust, just as the closely related element carbon is the chief constituent of organic bodies. The oxide of silicon (silica) occurs both free and in combination with bases as the various natural silicates.

Preparation of silicon.—When gaseous silicon tetrafluoride, SiF_4 (page 196), is passed into water, the reaction that takes place may be represented thus:



The element silieon may be obtained by heating the potassium salt of this hydrofluosilieie acid with the metal potassium.



Prepared in this way, silicon is obtained as a dark brown amorphous powder. It may, however, be obtained in the crystalline condition by heating for some time the same ingredients, with the addition of the metal zine; on cooling, an ingot of zine is obtained with crystals of silieon embedded in it; by treating this with hydrochlorie acid, the zine is dissolved, leaving very hard steel-grey crystals; there seems, however, to be some doubt as to this substance being pure silicon. Silicon forms an inflammable gas with hydrogen (SiH_4) and combines, when heated with dry hydrogen chloride, to form SiHCl_3 . These two substances have formulæ analogous to marsh gas (CH_4) and chloroform (CHCl_3).

SILICA

Formula, SiO_2 .

Also known as *oxide of silicon* and *silicic anhydride*.

Siliea occurs in the free state in nature as *rock crystal* (usually in six-sided prisms), *quartz*, *flint*, *sand*, *sandstone*, *agate*, *opal*, *jasper*, and *amethyst*. The so-called *infusorial earth*, or the inorganic remains of certain infusoria, consists essentially of amorphous siliea. Siliea is also present in the stems of certain grasses, cereals, and rushes, and in the feathers of many birds. Siliea is insoluble in water and in all acids execept hydrofluoric. Fused with the strong alkali bases, it forms salts, and thus reacts as an acid-forming oxide.

SILICIC ACID

Two varieties of silicic acid—metasilicic acid (H_2SiO_3), and orthosilicic acid (H_4SiO_4), have already been mentioned (page 62). The gelatinous substance formed in the reaction between silicon tetrafluoride and water (page 213) is perhaps our nearest approach to orthosilicic acid. A dilute aqueous solution of silicic acid may be obtained by dialysis (page 99), by acidulating with hydrochloric acid a dilute solution of soluble glass (page 216). The alkaline chloride and hydrochloric acid are crystalloids and pass through; the silicic acid remains in the dialyser.

Natural silicates.—Silicates, like carbonates, exist in quantity in nature, but their constitution is, as a rule, complex and somewhat uncertain. *Clay*, or aluminium silicate ($\text{Al}_2\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O}$), is the most widely distributed of the natural silicates; the colour of common or brown clay is due to iron contained in it. Clay in its purest form occurs as *kaolin* or *china-clay*, and is produced from felspar, a double silicate of aluminium and potassium, by the action of the carbon dioxide of the air, which unites with the potassium to form potassium carbonate; this is washed away, leaving the silicate of aluminium in a white state.

Amongst other silicates may be named *meerschau*m, *French chalk*, *asbestos*, *pumice*, etc.

Pure silica can be obtained from sand and from most silicates by fusing with three to four times its weight of sodium carbonate in a platinum dish and extracting the fused mass with water; on adding hydrochloric acid to the clear solution, silicon hydroxide ($\text{Si}(\text{OH})_4$) is precipitated in gelatinous flocks. This is filtered off, washed, and made red hot, when it is left as pure white silica (SiO_2).

Glass.—Glass may be defined as an amorphous mixture of various silicates nearly insoluble in water. Glass contains (1) silica, (2) soda or potash, (3) lime or lead oxide.

Crown glass, common window glass, bottle glass, or soda glass is made by fusing together chalk (CaCO_3), sodium carbonate (Na_2CO_3), and sand (SiO_2). It consists of calcium and sodium silicates. The green colour of common bottle glass is due to iron derived from the sand, and existing in the glass as ferrous silicate; the colour can be removed by adding to the melted glass a small quantity of manganese dioxide, which oxidises the green ferrous silicate to the almost colourless ferric silicate.

Hard glass or potash glass contains potassium in the place of sodium, and is made by fusing together chalk, potassium carbonate, and sand. It consists of calcium and potassium silicates, and requires a much higher temperature to melt it than soda glass; it is therefore useful in the manufacture of hard glass-tubing, and of chemical apparatus required to stand a high temperature.

Flint glass or crystal glass is a potash glass containing lead in the place of calcium, and is made by fusing together potassium carbonate (K_2CO_3), litharge or lead oxide (PbO), and sand (SiO_2). It consists of potassium and lead silicates, and is distinguished by its lustre and refractive power, hence it is valuable for optical purposes.

Soluble glass is either sodium or potassium silicate, generally the former. The sodium silicate is prepared by fusing together sodium carbonate and sand. It is a thick, syrupy liquid, miscible with, or soluble in, water; if painted over a surface, such as a wall, it is decomposed by the carbon dioxide of the air, a film of silica, or of a silicate, being left as a hard protective surface on the wall.

Coloured glasses are made by the addition of different metallic oxides to glass while in a molten condition. Blue glass is made by adding oxide of cobalt; red glass by adding cuprous oxide.

Porcelain and earthenware.—Porcelain and earthenware articles consist of clay that has been moulded into the required shapes, then baked hard, and afterwards covered with some substance that fuses at a high temperature, and forms a glaze, thus preventing the passage of liquids through what would otherwise be a porous medium. The glaze used for the finer kinds of porcelain is generally produced by dipping the unglazed article into water containing powdered felspar suspended in it; on draining the article the water sinks into the porous substance, leaving a film of felspar over its surface, and on strongly heating the article in a furnace this film of felspar melts and forms the glaze. Common earthenware, which is of a reddish-brown colour, is frequently glazed with litharge (oxide of lead), which forms an easily fusible lead silicate on the application of heat, this lead silicate constituting the glaze. If acid articles of food, such as vinegar, lemon-juice, lime-juice, etc., be kept in such vessels, the lead may be dissolved by the acid, and so the glaze may become a source of lead poisoning. Another very perfect glaze is salt glaze; common salt (sodium chloride) is thrown into the furnace containing the strongly-heated articles, the sodium chloride volatilises and is decomposed by the intense heat and the water vapour in the furnace. The sodium oxide formed condenses on the surface and forms with the clay a fusible silicate of sodium and aluminium. Borax is a common ingredient in glazes.



BORON

Symbol, B ; triad ; atomic weight, 11.

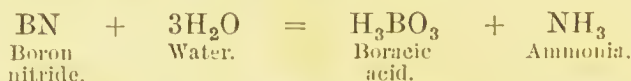
Boron does not occur in nature in the free state, but is found as free boric acid, and also in the form of various natural borates. In some respects its compounds resemble those of the metal aluminium.

Preparation of boron.—Amorphous boron is obtained, as a brown powder, by heating boron trioxide (B_2O_3) with sodium. Crystalline boron is prepared by melting the amorphous variety in aluminium, and when cold dissolving away the aluminium; it has been found to be a compound of aluminium and boron.

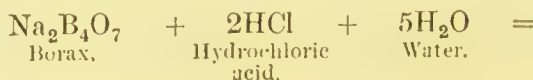
BORIC OR BORACIC ACID

Formula, H_3BO_3 .

Boric acid is found in the jets of steam known as *soffioni* issuing from fissures in the earth in the volcanic districts of Tuscany; these jets of steam condense and form small lagoons, by the concentration of the water of which boric acid is obtained. Since this volcanic boric acid is always accompanied by salts of ammonia, it is possible that it is produced deep down in the earth by the contact of boron nitride with steam, as these two bodies are known to decompose one another, as follows:—



Boric acid may also be prepared by mixing together a concentrated hot solution of borax with sulphuric or hydrochloric acids; on cooling, the boric acid crystallises out.





Properties.—Boric acid is a white solid, crystallising in small, soapy-feeling crystals, very soluble in hot, and moderately soluble in cold water. It possesses antiseptic properties, and is used as an antiseptic dressing and as a preservative.

On gently heating boric acid, each molecule of the acid loses a molecule of water, and metaboric acid is formed.



If further heat be applied, pyroboric acid ($\text{H}_2\text{B}_4\text{O}_7$) is produced, and finally all the water is driven off and boric anhydride or boron trioxide (B_2O_3) is left, thus :



Tests.—1. If boric acid be mixed with some alcohol, and a light applied to the mixture, the boric acid communicates a green colour to the flame of the burning alcohol.

2. If yellow turmeric paper be dipped into a solution of boric acid and dried at 100° , it turns reddish brown. On adding ammonia the colour turns dark blue. It is the only acid that turns turmeric brown, this colour being usually produced by alkalis.

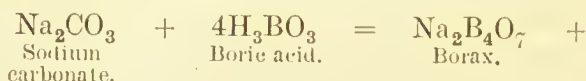
BORAX

Formula, $\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$.

This is pyroborate of sodium. Borax occurs native as *tinca* in Persia and elsewhere ; of late, borax has been found in large quantities in California.

Preparation of borax.—If the crude volcanic

boric acid be heated with sodium carbonate, ammonium carbonate volatilises (*see* page 165), and borax remains.



Borax when heated gives off its water of crystallisation, swelling up enormously (*intumescence*), and then melts. Fused borax dissolves many metallic oxides, and often acquires thereby characteristic colours; thus, cobalt gives a blue borax bead, chromium a green bead, etc. For the same reason it is largely used in the operation of "brazing," for uniting pieces of brass, silver, gold, etc.; the melted borax dissolves any oxide, and offers a clean metallic surface to which the solder adheres.

Tests.—1. If sulphuric acid be added to borax (to set free boric acid), the mixture stirred with alcohol, and a light applied, a green-coloured flame will be obtained.

2. If to a solution of borax, hydrochloric acid be added, the solution will give the turmeric paper test (*see* page 219).

To test for boric acid or borax in foods, we must first destroy the organic matters, but as heat would volatilise the boric acid in presence of moisture, we add a little sodium carbonate solution or lime-water to form the sodium or calcium salt. This will not be driven off by heat, and we can now evaporate to dryness and heat the dry residue till the organic matter is destroyed and a nearly white ash remains. Dissolve this ash in a small quantity of hydrochloric acid, filter the solution, and to the filtrate apply the turmeric test already described.

CHAPTER X

PHOSPHORUS—COMPOUNDS OF PHOSPHORUS

Phosphorus — Allotropic Forms — Phosphorus Oxide — Phosphorus Pentoxide — Phosphoric Acid — Pyrophosphoric Acid — Metaphosphoric Acid — Phosphorous Acid—Hypophosphorous Acid—Compounds of Phosphorus with Hydrogen—Compounds of Phosphorus with Chlorine—Compounds of Phosphorus with Bromine and Iodine—The Nitrogen Group of Elements.

PHOSPHORUS

Symbol, P ; molecule, P₄ ; pentad ; atomic weight, 31 ; molecular weight, 124.

PHOSPHORUS and arsenic are the only two elements that contain four atoms in the molecule ; the density of phosphorus vapour is 62, therefore its molecular weight is $62 \times 2 = 124$, and as the relative weight of its atom is 31, the molecule must contain four atoms (*see also* page 44).

Phosphorus (from *φῶς*, light ; *φέρειν*, to bear) derives its name from its property of shining, or being luminous, in the dark ; it occurs in nature principally as calcium phosphate in the minerals *apatite* and *phosphorite*, and in soils in small quantities. Plants possess the power of abstracting the calcium phosphate from soils, and of storing it in their tissues, partly in the form of a soluble calcium phosphate, and partly in the form of complex organic bodies containing phosphorus ; animals, by using plants as foods, convey phosphorus into their systems,

and the calcium phosphate, becoming deposited in bones, constitutes the principal inorganic and hardening constituent of them, whilst phosphorus in the form of complex organic bodies is an essential constituent of the brain, nervous, and other tissues. In our food more phosphorus is taken than the system requires, the excess being got rid of mainly by excretion as phosphates (principally in the urine, partly in the fæces), and thus returned to the soil. Phosphorus was first prepared (1674) from the calcium phosphate obtained from concentrated urine; later, the discovery was made that bones also contain calcium phosphate, and it is from this source that phosphorus is now prepared.

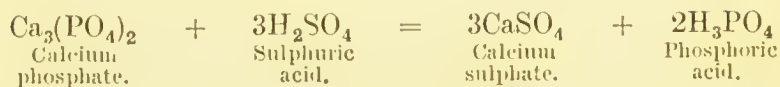
There are two allotropic forms of phosphorus, the *ordinary* or *yellow*, and the *red* or *amorphous*.

ORDINARY OR YELLOW PHOSPHORUS

This is prepared from bones in the following manner :—

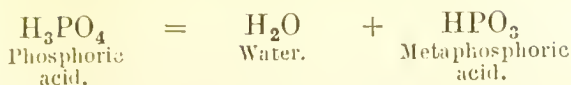
1. The bones are calcined to obtain bone-ash, an impure calcium phosphate.

2. The bone-ash is digested with sulphuric acid. Phosphoric acid remains in solution and calcium sulphate is precipitated.

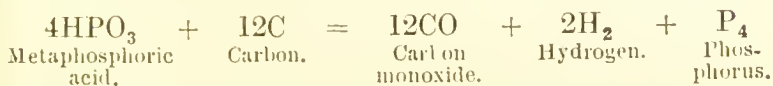


The liquid is filtered and evaporated to a syrup; 25 per cent. of charcoal powder is added, and the mixture dried; it is finally distilled at a red heat from clay retorts, and the phosphorus vapour collected under water.

The reactions which occur are: (a) the phosphoric acid gives off water and is converted into metaphosphoric acid.



(b) The metaphosphoric acid is reduced by the red-hot carbon.



3. The phosphorus so obtained is purified by forcing it, when melted under hot water, through wash-leather; the purified phosphorus is then cast into sticks, and kept under cold water.

Phosphorus is now largely prepared directly from calcium phosphate. A mixture of heated phosphate, carbon, and various fluxes is introduced into an electric furnace; the current is then turned on and the phosphorus vapour distils over. No sulphuric acid is required, and the process is continuous.

Properties.—Phosphorus is a colourless transparent solid when first prepared, somewhat resembling white wax in appearance and consistency, but it gradually becomes yellowish in colour by keeping. It melts at 44° (110° F.), ignites at a slightly higher temperature, boils at 290° , and out of contact with air or oxygen may be distilled unchanged; it is luminous in the dark, giving off white fumes of the oxide. Phosphorus is very apt to catch fire, and it is therefore kept under water. It is slightly soluble in ether and in the fixed oils, and is very soluble in carbon bisulphide; if its solution in this substance be poured on a sheet of paper or on the floor, the carbon bisulphide rapidly evaporates, and the phosphorus is left in so fine a state of division that it ignites spontaneously in a very short time. Phosphorus is very poisonous, and is a common constituent of *rat-pastes*.

Test.—The method most frequently employed

in toxicological analysis for the detection of free phosphorus is based upon the volatility and luminosity of the element. The material to be tested is placed in a flask with water acidulated with sulphuric acid. The flask is then connected with a condenser and the liquid distilled, the whole apparatus being placed in the dark. A flickering, luminous ring will soon appear if free phosphorus is present. (N.B.—Certain volatile substances interfere with this test.)

RED OR AMORPHOUS PHOSPHORUS

This is prepared by heating ordinary phosphorus in an atmosphere of carbon dioxide or of nitrogen to 240° for some time, any ordinary phosphorus which remains unchanged being removed by dissolving it out with carbon disulphide. It is also very slowly formed by the exposure to light of a stick of phosphorus, kept under water, when, after some time, a red coating of amorphous phosphorus forms on the stick.

If amorphous phosphorus be heated (while in an atmosphere of carbon dioxide or of nitrogen) to a high temperature, it passes into vapour which condenses as ordinary phosphorus.

Properties.—This allotropic form of phosphorus is a red-brown powder ; it was at one time universally regarded as amorphous, but appears to be not entirely without crystalline form of microscopic dimensions ; it does not fume in the air, nor is it luminous in the dark ; it does not melt at 250° , and catches fire only at 260° , so that there is no necessity for keeping it under water ; it is insoluble in carbon bisulphide, and all liquids ; it is odourless and non-poisonous.

Use of phosphorus in lucifer matches.—

Both varieties of phosphorus are used in the manufacture of lucifer matches. Common matches are tipped with a mixture containing ordinary phos-

phorus, and ignite when rubbed on any rough surface, the friction producing sufficient heat to set the phosphorus on fire. *Safely matches* have no phosphorus on their tips, but are tipped with a mixture of potassium chlorate, red lead, and black sulphide of antimony, the phosphorus being on the side of the box in the form of amorphous phosphorus, stuck on with common glue; when a safety match is rubbed against this, the portion of amorphous phosphorus rubbed adheres to the tip of the match and causes it to catch fire.

The following table contrasts the different properties of the two allotropic forms of phosphorus:—

ORDINARY PHOSPHORUS	AMORPHOUS PHOSPHORUS
<i>Form.</i> —In sticks.	In powder.
<i>Colour.</i> —Colourless, or yellow.	Red-brown.
<i>Odour.</i> —Peculiar.	None.
<i>Luminosity.</i> —Luminous in dark.	Not luminous.
<i>Inflammability.</i> —Ignites at 45° C., and is apt to ignite when handled.	Ignites at 260° C., and may be handled with impunity.
<i>Exposure to air.</i> —White fumes evolved.	No fumes evolved.
<i>Solubility.</i> —Soluble in carbon bisulphide, and slightly so in ether and the fixed oils.	Insoluble in all liquids.
<i>Physiological action.</i> —Very poisonous.	Not poisonous.

COMPOUNDS OF PHOSPHORUS AND OXYGEN

Three oxides of phosphorus are known—viz. phosphorous oxide or phosphorous anhydride (P_4O_6), phosphoric oxide or phosphoric anhydride (P_2O_5),

and phosphorus tetroxide (P_2O_4). Only the first two need be described here.

PHOSPHOROUS OXIDE

Formula, P_4O_6 .

When phosphorus is burnt in a rapid current of air a mixture of the two oxides P_4O_6 and P_2O_5 is formed; the mixture is passed through a glass tube surrounded with hot water at 60° ; the P_2O_5 condenses in this tube, while the more volatile P_4O_6 passes on and is condensed in a U-tube surrounded with a freezing mixture. It is a soft, waxlike, crystalline solid, melting at 22.5° ; it boils at 173° in an atmosphere of nitrogen or carbon dioxide; it gives off a very poisonous vapour. When warmed in oxygen it bursts into flame. Its vapour density is 110, and its molecular weight 220.

PHOSPHORUS PENTOXIDE

Formula, P_2O_5 .

This oxide is obtained as a white powder by burning phosphorus in oxygen, or in a free supply of air. At a high temperature it can be volatilised; it has a very powerful attraction for moisture, being one of the most hygroscopic substances known. It is the anhydride of phosphoric acid, and if dissolved in hot water it forms phosphoric acid at once; if dissolved in cold water it forms at first metaphosphoric acid; the metaphosphoric acid then gradually unites with more water to form ordinary phosphoric acid (*see* page 128).

ACIDS OF PHOSPHORUS

There are several acids of phosphorus, and five of these will be mentioned here. The origin and

constitution of some has already been indicated (page 63).

H_3PO_2 Hypophosphorous acid.

H_3PO_3 Phosphorous acid.

H_3PO_4 Phosphoric acid, or orthophosphoric acid.

HPO_3 Metaphosphoric acid.

$\text{H}_4\text{P}_2\text{O}_7$ Pyrophosphoric acid.

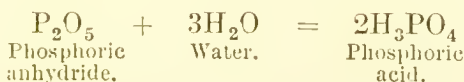
PHOSPHORIC, OR ORTHOPHOSPHORIC ACID

Formula, H_3PO_4 .

This is the ordinary or common phosphoric acid, and is called orthophosphoric acid (*ὀρθός*, true) in order to distinguish it from subordinate derivatives —e.g. metaphosphoric acid.

The name might perhaps with more propriety have been assigned to the hypothetical acid, the maximum hydroxide, H_5PO_5 (see page 63).

Modes of preparation. — 1. By dissolving phosphoric anhydride in water and boiling the solution.

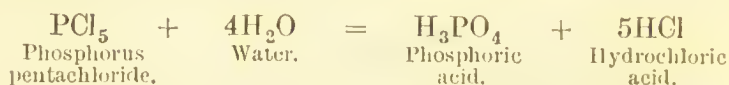


2. The phosphoric acid used in medicine is obtained by boiling together for some time phosphorus, nitric acid, and water; the phosphorus is oxidised by the nitric acid to phosphoric anhydride, and this with the boiling water forms phosphoric acid.



3. Phosphoric acid may be obtained by the action of phosphorus pentachloride on water, the hydro-

chloric acid being driven off by subsequent evaporation.



4. By the action of sulphuric acid on bone ash (*see* page 222).

Properties.—Phosphoric acid is one of the least volatile inorganic acids. The pure anhydrous acid is a crystalline solid melting at about 40° . The concentrated acid of the B.P. is a colourless syrupy liquid with an acid taste and reaction, and contains 66.3 per cent. of the pure compound. The acid is tribasic and forms three sodium salts, viz. Na_3PO_4 , Na_2HPO_4 , and NaH_2PO_4 , in aqueous solution; the last-mentioned salt is acid to test-paper, but the others are alkaline.

Tests.—1. Phosphoric acid when neutralised with ammonia gives a canary-yellow precipitate of silver phosphate with solution of silver nitrate; this precipitate is readily dissolved, both by solution of ammonia and by nitric acid.

2. If to phosphoric acid excess of ammonia be added, and then solutions of ammonium chloride and magnesium sulphate, a white crystalline precipitate will form on shaking the mixture; this precipitate is the magnesium ammonium phosphate (MgNH_4PO_4).

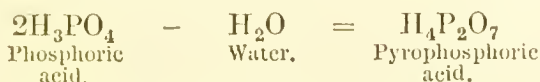
3. If a small quantity of a phosphate be boiled with strong nitric acid and ammonium molybdate, a bright-yellow precipitate is formed.

PYROPHOSPHORIC ACID

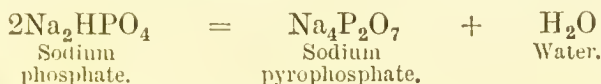
Formula, $\text{H}_4\text{P}_2\text{O}_7$:

This derivative of phosphoric acid is obtained by heating that acid a little above 200° ; two mole-

cules of phosphoric acid lose one molecule of water, forming pyrophosphoric acid.



It may also be obtained in the form of its sodium salt by heating ordinary sodium phosphate, thus :



Tests.—1. When neutralised with ammonia, pyrophosphoric acid gives a white precipitate with silver nitrate, thus distinguishing it from phosphoric acid, which gives a yellow precipitate.

2. Pyrophosphoric acid does not coagulate albumen, and it is thus distinguished from metaphosphoric acid (*see below*).

METAPHOSPHORIC ACID

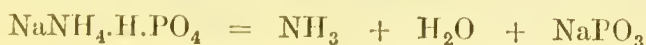
Formula, HPO₃.

This variety of phosphoric acid can be prepared by heating that acid to redness; one molecule of phosphoric acid loses one molecule of water, forming metaphosphoric acid, thus :



Metaphosphoric acid is obtained as a vitreous mass, and hence is known as *glacial phosphoric acid*; it dissolves in water, and its solution changes slowly at ordinary temperatures, but rapidly with heat, into ordinary phosphoric acid.

When microcosmic salt (page 279) is heated, sodium metaphosphate is obtained :



Tests.—1. When neutralised with ammonia, metaphosphoric acid gives a white precipitate with silver nitrate, and is thus distinguished from ordinary phosphoric acid, which gives a yellow precipitate.

2. If some unboiled white of egg be shaken with metaphosphoric acid, the albumen is coagulated; this test distinguishes metaphosphoric acid from pyrophosphoric acid, which does not possess the power of coagulating albumen.

PHOSPHOROUS ACID

Formula, H_3PO_3 .

In this acid phosphorus is only using a valency of three (page 64).

Modes of preparation.—1. By dissolving phosphorous oxide in cold water.



2. By the action of phosphorus trichloride on water.



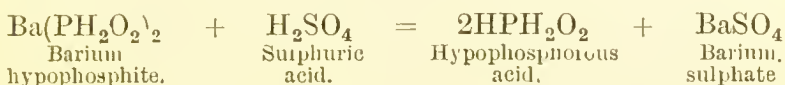
Properties.—Phosphorous acid has a very strong attraction for oxygen, and if exposed to the air forms phosphoric acid; on account of its affinity for oxygen it is a powerful reducing agent.

HYPOPHOSPHOROUS ACID

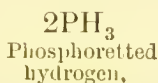
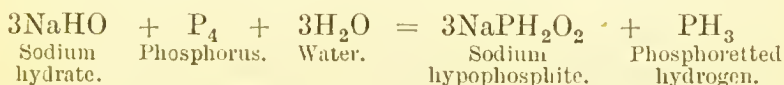
Formula, H_3PO_2 or HPH_2O_2 .

This acid contains one atom of oxygen less in the molecule than phosphorous acid; it is a monobasic acid, and its constitutional formula is therefore HPH_2O_2 . It may be prepared by decomposing its

barium salt (barium hypophosphite) with sulphuric acid, and filtering from the insoluble barium sulphate.



Preparation of the hypophosphites.—The sodium, potassium, calcium, and barium hypophosphites are prepared by boiling respectively the alkaline hydrate of the metal with phosphorus and water; in each case gaseous phosphoretted hydrogen is evolved. The two hypophosphites most employed in medicine are those of sodium (page 280) and calcium (page 290). Their preparation is shown in the following equations:



Tests.—1. The dry **hypophosphites**, when heated, evolve an inflammable gas, phosphoretted hydrogen (page 232).

2. Aqueous solutions of hypophosphites, when acidulated with dilute sulphuric acid, act as powerful reducing agents; they reduce mercuric salts to mercurous, cupric salts to cuprous, and even throw down a reddish precipitate of cuprous hydride (Cu_2H_2). If the respective test solutions are well boiled, mercury and copper are finally obtained. These solutions also discharge the colour of a solution of potassium permanganate (page 77).

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN

There are three compounds of these elements, a gas (PH_3), a liquid (P_2H_4), and a solid. The simplest formula of the solid is P_2H ; the molecular weight, and therefore the molecular formula, are not known.

GASEOUS PHOSPHORETTED HYDROGEN, OR PHOSPHINE

Formula, PH_3 .

Modes of preparation. — 1. As described above, this compound is produced when phosphorus is boiled with an alkali and water. The gas that is evolved is not, however, quite pure, since on coming into contact with the air it ignites spontaneously, whereas pure gaseous phosphoretted hydrogen is not spontaneously inflammable. Its spontaneous inflammability, when prepared by the action of phosphorus on an alkali, is due to its being contaminated with a small quantity of the vapour of the liquid phosphoretted hydrogen, which is spontaneously inflammable.

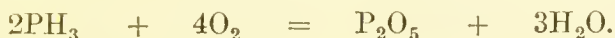
2. The pure gas is obtained by the action of potassium hydroxide upon phosphonium iodide.



It will be noticed that this equation is comparable with that on page 160, by which ammonia is prepared. In fact, phosphine resembles ammonia in several respects: thus it combines directly with hydrogen chloride, bromide, and iodide to form salts by *addition* (PH_4Cl , etc.), but it is not so strongly basic as ammonia.

Properties. — The specific gravity of phosphoretted hydrogen is 17, and it is somewhat heavier

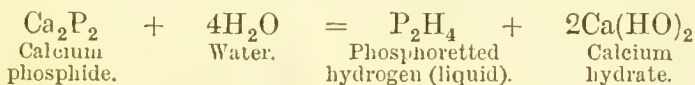
than air; it is a colourless gas, with a very unpleasant garlic-like odour, nearly insoluble in water, and igniting when a light is applied to it, forming by its combustion phosphorus pentoxide and water.



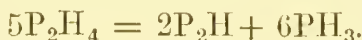
LIQUID PHOSPHORETTED HYDROGEN

Formula, P_2H_4 .

Preparation.—This body is obtained, mixed with PH_3 , by the action of calcium phosphide on water.



Properties.—A liquid possessing a very unpleasant odour, and catching fire spontaneously on exposure to the air; it is very unstable, especially if exposed to sunlight, decomposing into the gaseous and solid phosphoretted hydrogen,]



Calcium phosphide is sometimes used as a signal at sea, since when thrown into water, the phosphoretted hydrogen evolved takes fire and burns with a bright light.

SOLID PHOSPHORETTED HYDROGEN

Empirical Formula, P_2H .

This body results, as already mentioned, from the decomposition of the preceding compound by light. It is a yellow powder, without taste or smell, and may be ignited by percussion or by heating to about 200° .

COMPOUNDS OF PHOSPHORUS WITH CHLORINE

Phosphorus forms two chlorides; they have already been mentioned (page 54).

PHOSPHORUS TRICHLORIDE, OR PHOSPHOROUS CHLORIDE

Formula, PCl_3 ; boiling point, 76° .

A colourless liquid, fuming in moist air, and produced by burning phosphorus in chlorine, keeping the phosphorus in excess. It is conveniently prepared by passing chlorine over red phosphorus moderately heated, and condensing the volatile chloride formed, by cooling the exit tube. Phosphorus trichloride is decomposed by water, with formation of phosphorous and hydrochloric acids.

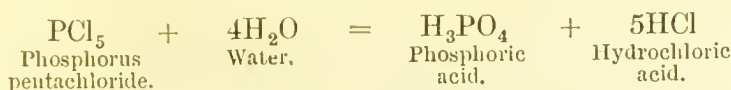


Chlorine converts phosphorus trichloride into the pentachloride.

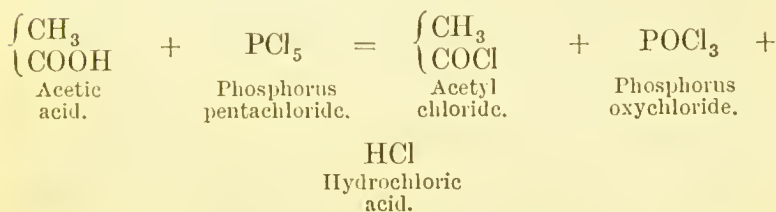
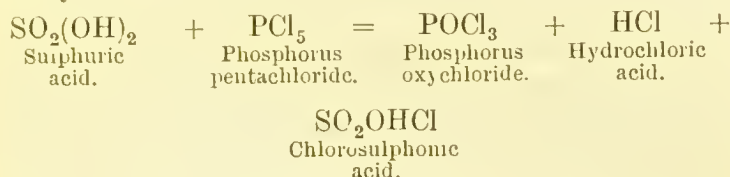
PHOSPHORUS PENTACHLORIDE, OR PHOSPHORIC CHLORIDE

Formula, PCl_5 .

A white crystalline body, volatilising and fuming in moist air. It is produced (1) by the action of chlorine on the trichloride of phosphorus; (2) by burning phosphorus in excess of chlorine; (3) by passing chlorine into a solution of phosphorus in carbon bisulphide. Phosphorus pentachloride is decomposed by water, with formation of phosphoric and hydrochloric acids.



Phosphorus pentachloride is an extremely useful reagent, since it acts upon organic and inorganic bodies containing the hydroxyl group, replacing the OH by Cl.



Formation of hydrochloric acid when phosphorus pentachloride acts on any substance is therefore evidence that the substance contains an hydroxyl group.

Phosphorus pentachloride has a vapour density at 300° of 52, instead of $(\text{PCl}_5 \ 31 + 177.5) \frac{208.5}{2} = 104.2$. This is explained by the fact that PCl_5 vapour does not exist; in ordinary conditions it dissociates into $\text{PCl}_3 + \text{Cl}_2$, so that we have two molecules, and must therefore divide the molecular weight by 4 instead of 2.

COMPOUNDS OF PHOSPHORUS WITH BROMINE AND IODINE

There are two bromides of phosphorus, a tri-bromide (PBr_3), which is a liquid body, and a penta-bromide (PBr_5), which is a solid body.

There are also two iodides of phosphorus, a diiodide (P_2I_4), and a tri-iodide (PI_3), both solid bodies.

All these compounds are produced by direct combination between the elements.

PBr_3 and PI_3 react with water, or other hydroxide, similarly to PCl_3 replacing the hydroxyl by Br and I respectively. HBr and HI are thus obtained.

The nitrogen group of elements.—Attention has already been called (page 232) to the fact that phosphine can be prepared by a reaction comparable to that by which we obtain ammonia. This is but one of many points of resemblance between the elements nitrogen and phosphorus. Resemblance has also been noticed (page 44) between phosphorus and arsenic, and the student will shortly find evidence of a very close resemblance between arsenic and antimony. In fact, the elements nitrogen, phosphorus, arsenic, antimony, and bismuth form a natural group, the fifth group of the periodic table (page 88). All (except bismuth) form gaseous hydrides having the formulæ NH_3 , PH_3 , AsH_3 , SbH_3 . We find also the corresponding anhydrides N_2O_5 , P_2O_5 , As_2O_5 , Sb_2O_5 ; the metallic nature of the elements becomes more marked as the atomic weight increases, so that the oxides of bismuth do not form well-marked acids. The same general resemblance and gradation are seen in the chlorides. NCl_3 is unstable to an explosive extent, PCl_3 and $AsCl_3$ are *completely* decomposed by water. $SbCl_3$ and $BiCl_3$ are *partially* decomposed by water, the oxychloride being obtained.

CHAPTER XI

SULPHUR—OXIDES, ACIDS, AND COMPOUNDS OF SULPHUR

Sulphur—Allotropic Forms—Sulphur Dioxide—Sulphur Trioxide—Sulphurous Acid—Sulphuric Acid—Nordhausen or Fuming Sulphuric Acid—Hydrogen Sulphide—Hydrogen Persulphide—Thiosulphuric Acid—Sodium Thiosulphate—Compounds of Sulphur with Chlorine

SULPHUR

Symbol, S ; hexad ; atomic weight, 32 ; molecular formula, see pages 44-46.

SULPHUR, commonly known as *brimstone*, occurs in nature in considerable quantities, in both the free and combined states. In the free state it is found in the volcanic districts of Sicily, Italy, and Iceland, in the form of yellow crystals, or in the amorphous state embedded in blue clay. In the combined state it exists as the various native metallic sulphides (*e.g.* iron pyrites FeS_2 , blende ZnS , black antimony Sb_2S_3 , copper sulphide CuS , galena PbS , cinnabar HgS), and as native metallic sulphates (*e.g.* gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Epsom salts $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, heavy spar BaSO_4). Sulphur is obtained from the rock, in which it occurs in volcanic districts, by melting it out ; it is purified by distillation, the sulphur being converted into vapour, which is conducted into a large and cool brick chamber, where it becomes cooled, and condenses, first to a yellow powder,

flowers of sulphur, which subsequently melts, and is cast into sticks.

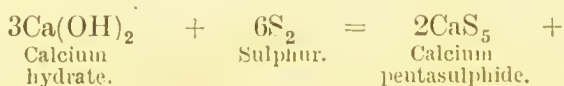
There are three allotropic forms of sulphur—viz. two crystalline forms (the octahedral and the prismatic) and an amorphous form.

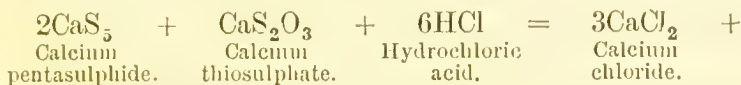
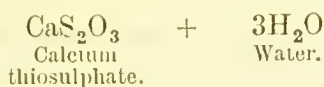
The allotropic forms of sulphur. 1.

Octahedral variety.—This is obtained by dissolving powdered stick sulphur in carbon bisulphide, and allowing the solution to evaporate spontaneously, when octahedral crystals of sulphur are deposited. Sulphur is found native crystallised in this form.

2. *Prismatic variety.*—This may be obtained by heating sulphur in a crucible until it melts, allowing it to cool until a crust forms on the surface, and then perforating the crust with an iron rod and pouring out the molten sulphur from underneath, when long prismatic crystals of sulphur will be found adhering to the sides of the crucible.

3. *Amorphous variety.*—This may be produced in two forms, plastic sulphur and precipitated sulphur. *Plastic sulphur* is prepared by heating sulphur to a temperature between 300° and 400° , and then pouring it into cold water, when it forms a plastic mass which can be drawn out like soft caoutchouc; it does not, however, retain its plasticity for long, as it gradually becomes hard and brittle, owing to its conversion into the crystalline condition. *Precipitated sulphur* is obtained by boiling flowers of sulphur with calcium hydrate (slaked lime) and water, when the sulphur passes into solution as calcium pentasulphide (CaS_5) and calcium thiosulphate (CaS_2O_3), from which solution the sulphur may be precipitated in the amorphous form by hydrochloric acid, which unites with the calcium and so sets free the sulphur.





This is the process for preparing the *precipitated sulphur* of the British Pharmacopœia. If sulphuric acid is used instead of hydrochloric acid, calcium sulphate will be produced instead of calcium chloride, and, since the calcium sulphate is insoluble, will be thrown down with the precipitated sulphur. This mixture of calcium sulphate and sulphur used to be known as *milk of sulphur*, formerly an official preparation in the Pharmacopœia, but its use has been discontinued on account of the large quantity of insoluble sulphate present in it.

Properties.—Sulphur is a solid, possessing a pale-yellow colour, odourless, tasteless, and insoluble in water; it burns with a pale-blue flame, producing sulphur dioxide or sulphurous anhydride, a gas having a very pungent odour. At about 115° sulphur melts to a clear mobile liquid, which, if allowed to cool, resolidifies to the ordinary yellow sulphur (the prismatic variety); if more strongly heated, it undergoes a peculiar change, for, instead of becoming more mobile, it becomes more viscid, and darker in colour, so that at 200° it is a dark brown liquid, and so sticky that the vessel containing it may be inverted without the sulphur flowing out; if heated above 200° , and up to 400° , it gradually becomes mobile again, and boils at about 444° . Sulphur unites directly with oxygen, chlorine, phosphorus, carbon, and most of the metals. Sulphur is soluble in carbon disulphide.

Test.—Its yellow colour, combined with its burning with a pale-blue flame, and producing the pungent-smelling gas sulphur dioxide, renders the recognition of free sulphur very easy.

COMPOUNDS OF SULPHUR AND OXYGEN

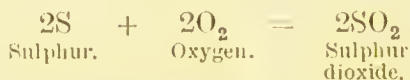
There are two oxides of sulphur, viz. a gaseous oxide, sulphur dioxide or sulphurous anhydride (SO_2), and a solid oxide, sulphur trioxide or sulphuric anhydride (SO_3).

SULPHUR DIOXIDE, OR SULPHUROUS ANHYDRIDE

SO_2 ; gas; *liquefies at* -10° ; *freezes at* -76° .

This compound is contained in the gases of volcanoes.

Modes of preparation.—1. By the combustion of sulphur in air or oxygen.



2. By roasting iron pyrites in air.

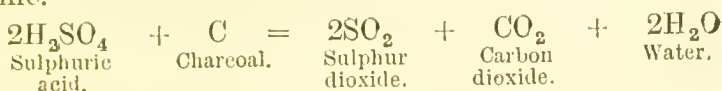


3. For experimental purposes sulphur dioxide is most readily prepared by the action of strong sulphuric acid with heat on the metals copper, silver, or mercury (*see* page 74).



4. Sulphur dioxide can be cheaply prepared by the action of strong sulphuric acid with heat on charcoal; it is not, however, pure, as it is mixed

with carbon dioxide, which is produced at the same time.



Properties.—The specific gravity of sulphur dioxide is 32, and it is considerably heavier than air; it is a colourless gas, with a very pungent irri-

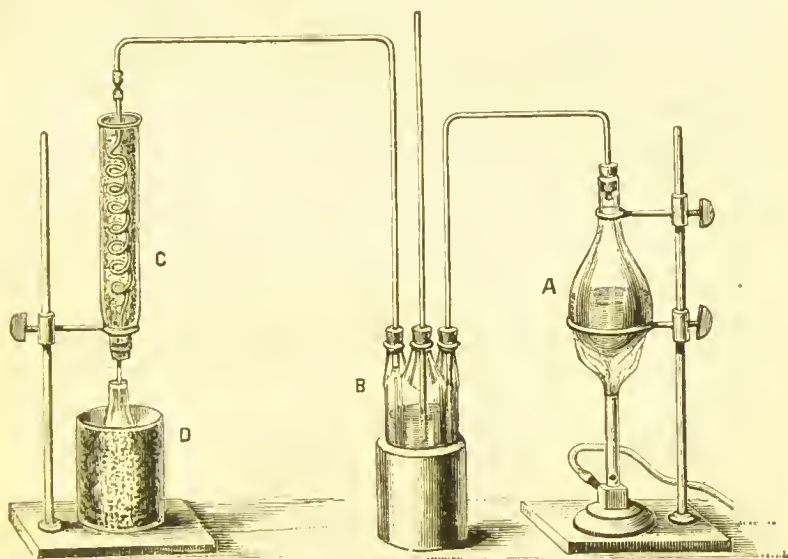


Fig. 28.—Preparation and liquefaction of sulphur dioxide.

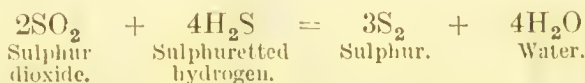
tating odour, and an acid taste; it is neither combustible nor is it a supporter of combustion; it is very poisonous, and is freely soluble in water, 60 volumes dissolving in 1 volume of water. If cooled by means of a freezing mixture it condenses to a liquid; the apparatus for liquefying it is shown in Fig. 28. A is a flask in which the sulphur dioxide is prepared by heating strong sulphuric acid with copper. The gas is passed through a wash-bottle B, and then through a spiral tube surrounded by a freezing mixture C, the liquefied gas being received

in a flask D, which is also surrounded by a freezing mixture. Sulphur dioxide is a reducing agent. It bleaches moist vegetable colours indirectly by reduction.



It is also an antiseptic, by virtue of its germicidal properties; as an antiseptic it is employed in the disinfection of rooms in which patients suffering from infectious fevers have been kept, but it is doubtful whether it is thoroughly reliable for such a purpose. For this purpose sulphur is heated in an iron saucepan until it has passed through the viscid stage and again become mobile (page 239); it is then lighted in the room, the windows and the doors being closed; 1 to $1\frac{1}{2}$ lb. of sulphur is used for every 1,000 cubic feet of air space in the room.

If sulphur dioxide and sulphuretted hydrogen gases be mixed, a cloud of free sulphur is formed.



It is possible that much of the sulphur found free in nature in volcanic districts is produced in this manner.

Tests.—1. Its peculiar pungent and irritating odour.

2. It turns paper moistened with potassium bichromate bluish green.

3. It gives a blue colour with a mixture of iodic acid and starch.

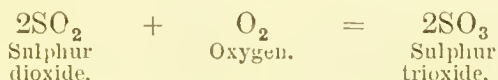
4. It decolorises an aqueous solution of potassium permanganate.

5. If an aqueous solution of the gas be neutralised with $\text{NH}_3\text{.Aq.}$ the neutral solution will respond to the tests for *sulphites* (page 244).

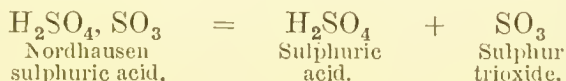
SULPHUR TRIOXIDE OR SULPHURIC ANHYDRIDE

Formula, SO₃ ; melts at 14·8° ; boils at 46·2°.

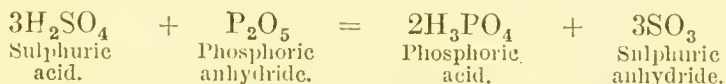
Modes of preparation.—1. By passing a mixture of sulphur dioxide and oxygen over heated and finely divided platinum, when the two gases unite to form the higher oxide of sulphur (*see catalysis, page 77*).



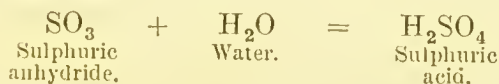
2. By gently heating Nordhausen or fuming sulphuric acid, when sulphuric anhydride volatilises over and condenses.



3. By distilling sulphuric acid with phosphoric anhydride.



Properties.—Sulphur trioxide is a solid body, occurring in white silky needles. It dissolves with avidity in water, uniting with it to form sulphuric acid.



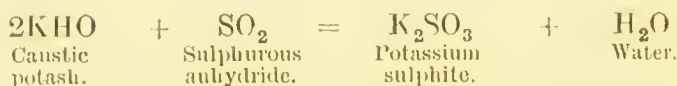
SULPHUROUS ACID

Formula, H₂SO₃.

Mode of preparation.—By passing sulphurous anhydride into water.



Properties.—Sulphurous acid possesses the characteristic pungent odour of sulphurous anhydride. If exposed to the air, oxygen is absorbed, and the sulphurous acid is slowly converted into sulphuric acid ($2\text{H}_2\text{SO}_3 + \text{O}_2 = 2\text{H}_2\text{SO}_4$). On account of this readiness to combine with oxygen, sulphurous acid is a powerful reducing agent. Nascent hydrogen can, however, reduce sulphurous acid, depriving it of all its oxygen, and setting free sulphuretted hydrogen ($\text{H}_2\text{SO}_3 + 3\text{H}_2 = \text{H}_2\text{S} + 3\text{H}_2\text{O}$). If sulphurous acid be neutralised with an alkaline hydrate or carbonate, a sulphite is produced. Sulphites are more easily prepared by the union of sulphurous anhydride with the strong bases; thus, if sulphurous anhydride be passed into solutions of caustic potash or caustic soda, sulphites of the metals are produced, as follows:



Tests.—1. If to a solution of a *sulphite* some hydrochloric acid be added, sulphurous acid is set free, and this can be readily detected on warming by the evolution of the pungent-smelling sulphur dioxide (see Tests, page 242).

2. If to sulphurous acid or a solution of a *sulphite* some zinc and hydrochloric acid be added, the nascent hydrogen will reduce the sulphurous acid to sulphuretted hydrogen (see above), which can readily be detected by its odour, and by its blackening a piece of filter-paper moistened with a solution of lead acetate.

3. If to an aqueous neutral solution of a *sulphite* some barium chloride solution be added, a white

precipitate is obtained which is insoluble in dilute acetic acid, but is soluble in dilute hydrochloric acid (distinction from sulphate).

SULPHURIC ACID

Formula, H_2SO_4 .

Modes of preparation.—Sulphuric acid is obtained by the oxidation of sulphurous acid. This may be effected, though very slowly, by exposing sulphurous acid to the air. Sulphuric acid is now manufactured on an enormous scale. Two processes are employed :—

1. The leaden chamber process.
2. The contact or catalytic process.

The *first process* consists in oxidising sulphurous acid to sulphuric acid in large leaden chambers, the oxidation being effected in the first place by means of nitric acid, and afterwards by means of nitrogen peroxide produced from the nitric acid and oxygen of the air. The leaden chambers, supported by means of an external wooden framework, are arranged in a series communicating with one another. Into the first one the flue of a furnace passes; the last one is connected with a tower. Fig. 29 represents the first of the leaden chambers. In the furnace A is burnt sulphur or iron pyrites (FeS_2), the resulting sulphur dioxide passing along with a current of air into the leaden chamber. At the commencement of the process a vessel containing some sodium nitrate and sulphuric acid is placed within the furnace on one side, so that the vapour of the nitric acid evolved passes with the current of sulphur dioxide and air into the leaden chamber; this vessel only requires re-charging occasionally. The boiler B discharges steam (instead of steam, water spray is often used) into the interior of the chamber, and at the bottom

of the chamber the sulphuric acid collects in a diluted condition, and is drawn off from time to time. The formation of the sulphuric acid takes place as follows :

1. The sulphur dioxide passing into the leaden chamber unites with the steam to form sulphurous acid.

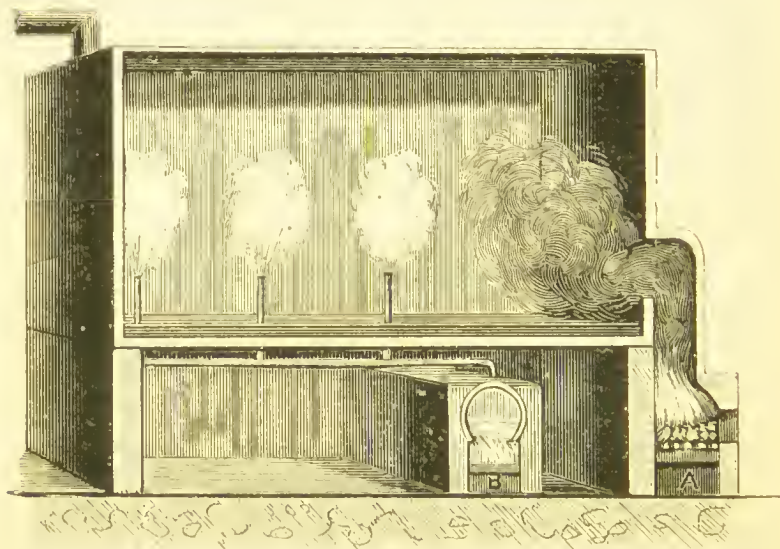
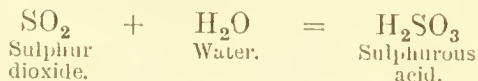
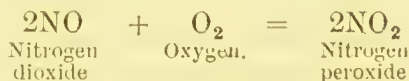


Fig. 29.—Sulphuric acid leaden chamber.

2. This sulphurous acid is immediately oxidised by the nitric acid vapour to sulphuric acid, nitrogen dioxide being evolved.



3. The nitrogen dioxide then unites with the oxygen of the air that has passed into the chamber to form nitrogen peroxide.



4. This nitrogen peroxide oxidises more sulphurous acid to sulphuric acid, nitrogen dioxide being again formed.



5. The nitrogen dioxide is again converted by the oxygen of the air into nitrogen peroxide, which then oxidises more sulphurous acid. It will be noticed, therefore, that in this lead-chamber process the oxidation of the sulphurous acid is effected in two different ways: (a) by means of nitric acid vapour, a small quantity only of which has to be generated from time to time to start the work of oxidation; (b) by means of the nitrogen dioxide, produced by the reduction of the nitric acid, acting as a carrier of the oxygen of the air to the sulphurous acid, by forming nitrogen peroxide; this, oxidising some of the sulphurous acid to sulphuric acid, reproduces nitrogen dioxide, which then carries on its work of combining with the oxygen of the air. The nitrogen dioxide is unable to continue this work for an indefinite period, on account of its being gradually swept away in the current that is passing through the leaden chambers; for, since the air that passes into the chambers contains four-fifths of its bulk of nitrogen, this nitrogen must pass away to make room for the fresh gases and air streaming in. As, with this escaping nitrogen, a considerable quantity of nitrogen peroxide must pass away, and as the latter gas would very seriously vitiate the atmosphere in the neighbourhood of the sulphuric-acid works if allowed to pass into it, some provision has to be made for the absorption of this gas. To effect this, the gases as they escape from the last of the series of leaden chambers are made to pass up a tall tower, known as a Gay-Lussac's tower, in which strong

sulphuric acid is kept slowly trickling down over pieces of coke; the nitrogen peroxide is absorbed by the strong sulphuric acid, from which it can be liberated by dilution, and so can be conducted into the first of the leaden chambers, to start its work of oxidation over again. The sulphuric acid that collects at the bottom of the leaden chambers is in a diluted condition; it is known as "chamber acid," and contains about 66 per cent. of H_2SO_4 ; it is concentrated by evaporation, at first in leaden vessels, and afterwards in glass or platinum vessels.

Large quantities of strong sulphuric acid are now made by the *contact* or *catalytic process* used in the laboratory on a small scale for the synthesis of sulphuric anhydride from sulphur dioxide and oxygen (page 243). Ferric oxide has been employed as the catalytic agent, in place of spongy platinum, in some works. In extending the laboratory method to a manufacturing scale, many practical difficulties were encountered, but they have been successfully overcome. The sulphuric anhydride when formed is absorbed in strong sulphuric acid.

Properties.—Sulphuric acid, which is commonly known as *oil of vitriol*, is one of the strongest acids; the pure commercial acid is of specific gravity 1.843, and contains 94 per cent. of sulphuric acid. If strong sulphuric acid is mixed with water, the mixture becomes extremely hot, owing probably to the formation of actual hydrates, including at least the compound (H_2SO_4 , H_2O). On account of its powerful attraction for water, strong sulphuric acid is employed for the purpose of drying those gases on which it has no chemical action. If sulphuric acid be allowed to drop on hot bricks, or pieces of heated pumice-stone, it is decomposed into water, sulphur dioxide, and oxygen ($2\text{H}_2\text{SO}_4 = 2\text{H}_2\text{O} + 2\text{SO}_2 + \text{O}_2$).

Commercial sulphuric acid is very apt to contain

small quantities of lead, arsenic, and nitrogen peroxide as impurities. The lead exists as the sulphate, and is derived from the leaden evaporating vessels in which the acid is concentrated. Although lead sulphate is soluble in strong sulphuric acid, it is not soluble in the dilute acid, and therefore comes down as a white precipitate on the strong acid being diluted with water. Arsenic is derived from iron pyrites being used as the source of the sulphur dioxide; arsenic may be detected in the sulphuric acid by diluting it with water, and passing a stream of sulphuretted hydrogen gas through it, when a yellow precipitate of sulphide of arsenic is produced if that impurity is present; or it may be detected by Marsh's test (see page 341). Sulphuric acid can be manufactured free from arsenic by employing Sicilian sulphur in the place of iron pyrites. Nitrogen peroxide is derived from the atmosphere of the leaden chambers; it can be detected by shaking the strong sulphuric acid with powdered ferrous sulphate, which will turn of a dark colour if any nitrogen peroxide be present. Sulphuric acid can be freed from this impurity by boiling with a few crystals of ammonium sulphate, when ammonium nitrite is formed, and immediately decomposed by the heat into nitrogen and water ($\text{NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O}$).

Test.—Sulphuric acid, or a soluble sulphate, gives with solution of barium chloride a white precipitate, insoluble in hydrochloric acid. All *sulphates* are soluble in water except lead sulphate, barium sulphate, and strontium sulphate. Calcium sulphate is only slightly soluble, but the solution is one of the common laboratory reagents.

NORDHAUSEN OR FUMING SULPHURIC ACID

This is a commercial form of strong sulphuric acid containing sulphuric anhydride in solution, the

fumes which it gives off on exposure to the air being caused by the liberation of this sulphuric anhydride. Its composition is usually indicated by the formula $\text{H}_2\text{S}_2\text{O}_7$. It is obtained by first drying crystallised ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), which loses six-sevenths of its water, having then the formula $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, and then strongly heating this dried ferrous sulphate in clay or earthenware retorts, when the fuming sulphuric acid distils over, ferric oxide (Fe_2O_3) being left in the retort. The fuming acid is now also made by the contact process.

SULPHURETTED HYDROGEN

Formula, H_2S ; liquefies at -62° ; freezes at -85° ; critical temperature, 100° .

This gas is analogous to water in its composition. The general analogy between sulphides and oxides has already been noticed (page 58).

Modes of preparation.—1. This gas is generally prepared for laboratory purposes by the action of hydrochloric acid or *dilute* sulphuric acid on sulphide of iron.



Small lumps of sulphide of iron are placed in a bottle (Fig. 30) with two tubulures, c, the bottom of the bottle is covered with broken glass up to the level AA, on this rests the sulphide of iron; acid is poured into the bottle B, which is connected with c by a flexible tube: on opening the tap T the acid flows into c, and a brisk evolution of the gas occurs; it

is then allowed to pass through some water in a wash-bottle, and thence into whatever solution it is required to be passed. When the tap *T* is closed the gas accumulates in *c* and forces the acid up into *B*, and the evolution of the gas ceases. As stated on page 204, the Kipp's apparatus (Fig. 25) is often employed to furnish a supply of the gas. The broken lumps of ferrous sulphide are placed in the bulb *B* and the acid is poured into *A*.

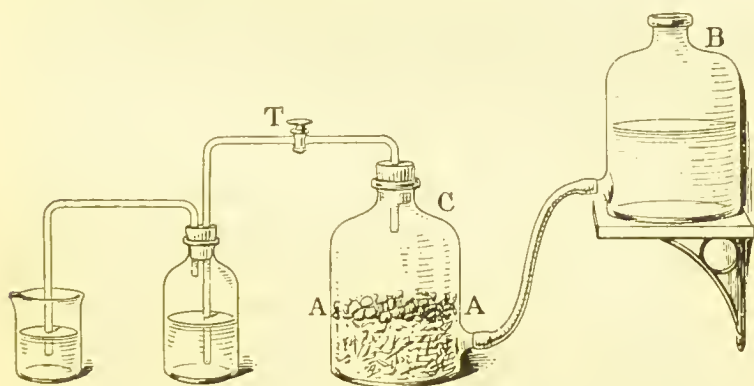


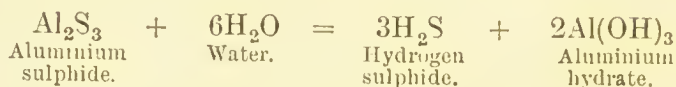
Fig. 30.—Apparatus for the supply of hydrogen sulphide.

2. It may also be prepared by the action of hydrochloric acid on the native sulphide of antimony.



3. Pure sulphuretted hydrogen, such as should be employed in toxicological inquiries, may be obtained by a method suggested by Divers: ordinary H_2S is passed into water containing magnesium hydroxide in suspension; the hydroxide is converted into hydrosulphide ($\text{Mg}(\text{SH})_2$) which dissolves; the clear fluid is poured into a flask furnished with a cork and delivery tube; on warming to $60\text{--}65^\circ$ pure hydrogen sulphide is evolved.

4. Another plan is to treat aluminium sulphide with water.



5. Sulphuretted hydrogen can be obtained in small quantities by direct union of its elements, as when hydrogen is passed over heated sulphur.

Properties.—The specific gravity of sulphuretted hydrogen is 17, and it is somewhat heavier than air; it is a combustible gas, burning with a pale blue flame, and producing sulphur dioxide and water; it is not a supporter of combustion. Sulphuretted hydrogen is a colourless gas, but possesses a peculiar and very disagreeable odour, similar to that of rotten eggs, and a sweetish unpleasant taste. Water at ordinary temperatures dissolves about three times its volume of the gas; but if the solution is kept in a bottle half full of air, the sulphuretted hydrogen is gradually decomposed by the oxygen of the air, sulphur becoming deposited ($2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + \text{S}_2$). A little glycerine added to the water tends to preserve the strength of the solution. Sulphuretted hydrogen is a poisonous gas; it can be liquefied by a pressure of 17 atmospheres at 10° . In a high state of dilution, sulphuretted hydrogen is contained in some mineral waters used for medicinal purposes—e.g. those of Harrogate and Aix-la-Chapelle; it is also evolved during the putrefactive decomposition of animal matter, eggs, etc.

The slow blackening of oil-paintings is due to the conversion of the white lead of the paint into the black sulphide of lead by slight traces of sulphuretted hydrogen in the air, these traces being derived partly from coal-gas and partly from minute quantities evolved from the human body. If chlorine is brought in contact with sulphuretted hydrogen, the disagree-

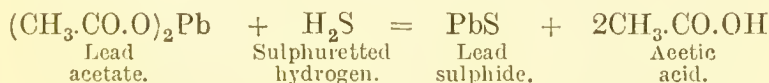
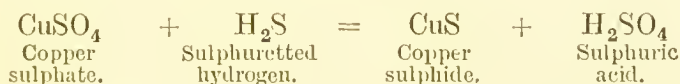
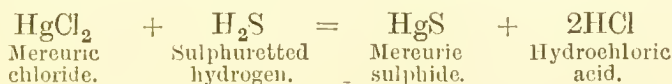
able smell of the latter immediately disappears, owing to the decomposition of the gas by the chlorine, with liberation of sulphur ($2\text{H}_2\text{S} + 2\text{Cl}_2 = 4\text{HCl} + \text{S}_2$). The metallie **sulphides** may be divided into three main groups:—

1. Those which are soluble in water, and are therefore not precipitated by sulphuretted hydrogen at all—e.g. calcium sulphide, sodium sulphide, etc.

2. Those which are insoluble in water, but soluble in dilute hydrochloric acid; these are precipitated in *neutral* solutions—e.g. zinc sulphide, ferrous sulphide.

3. Those which are insoluble in dilute hydrochloric acid, and are therefore precipitated even in acid solutions.

On this account, the gas is of great use in the separation of the metals for analytical purposes. The following equations illustrate the action of sulphuretted hydrogen on certain metallie salts:—



Sulphuretted hydrogen is a powerful reducing agent: it reduces ferric salts to ferrous salts, acid solution of potassium bichromate to green chromium salts, etc.; in all such reactions sulphur is precipitated.

Test.—Apart from its odour, which is very characteristic, sulphuretted hydrogen may be detected by its blackening a piece of filter-paper that has been dipped in a solution of lead acetate; the darkening

is due to the formation of the black sulphide of lead.

HYDROGEN PERSULPHIDE

Formula, H_2S_2 .

This body is analogous to hydrogen peroxide (H_2O_2) in its composition. It may be obtained by pouring a solution of potassium pentasulphide (K_2S_5) into strong hydrochloric acid, when, in addition to the liberation of sulphuretted hydrogen and sulphur, a heavy oily liquid sinks to the bottom, which is the persulphide of hydrogen in a somewhat impure condition. It is a very unstable body, readily decomposing into sulphuretted hydrogen and sulphur.

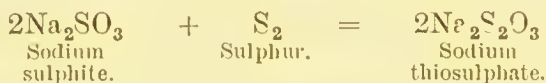
THIOSULPHURIC ACID

Formula, $H_2S_2O_3$.

This acid is not known in the free state, but only in its salts, of which the most important is sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$), commercially known as *hyposulphite of soda*.

Preparation of sodium thiosulphate.—

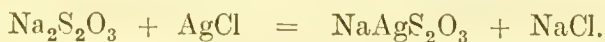
1. By warming together for some time a solution of sodium sulphite and powdered sulphur.



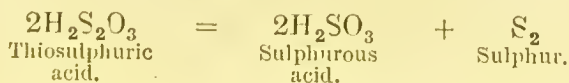
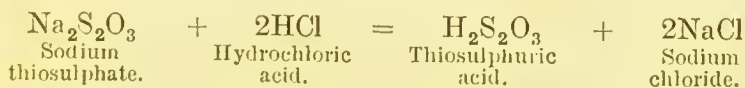
2. If sulphur dioxide be passed into calcium sulphide (the alkali-waste obtained in the manufacture of sodium carbonate), it is partly converted into calcium thiosulphate (CaS_2O_3), which by treatment with sodium carbonate yields the soluble sodium thiosulphate and the insoluble calcium carbonate.



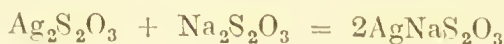
Properties.—Sodium thiosulphate is so named because it is regarded as sodium sulphate (Na_2SO_4) from which one atom of oxygen is withdrawn and an atom of sulphur (*θειον*, sulphur) substituted for it. It is largely employed (under the commercial name of hyposulphite of soda) in photography, on account of the property that it possesses of dissolving the bromide, iodide, and chloride of silver, provided these compounds have not been changed by the action of light; a sensitive photographic plate is covered with a thin layer of one or more of these silver compounds, which becomes decomposed on those parts only on which the light has fallen; after *developing* (see page 387) the picture, the silver salt that remains unchanged is removed by immersing the plate in a solution of hyposulphite of soda. This is called “fixing” the photograph; it depends upon the formation of a double salt of sodium and silver, NaAgS_2O_3 , which is soluble in water.



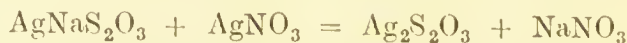
Tests.—1. If to a solution of sodium thiosulphate some hydrochloric acid be added, the smell of sulphur dioxide is evolved, and sulphur is precipitated after the solution has stood for a short time. This reaction is due to the liberation of thiosulphuric acid, which, being extremely unstable, is quickly decomposed into sulphurous acid and sulphur, the former evolving sulphur dioxide, which is known by its odour.



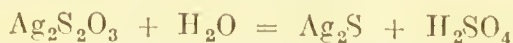
2. The addition of silver nitrate solution to a solution of sodium thiosulphate produces effects which are quite characteristic and deserve notice. A transient precipitate of $\text{Ag}_2\text{S}_2\text{O}_3$ first appears, but rapidly dissolves in excess of the sodium salt forming the soluble AgNaS_2O_3 , thus :



But when sufficient AgNO_3 has been added, the insoluble silver thiosulphate persists, thus :

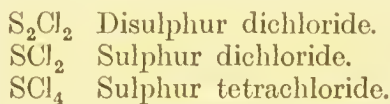


This precipitate is almost white at first, but rapidly darkens, especially if warmed, becoming brown and finally black, owing to its conversion to silver sulphide (Ag_2S), thus :



COMPOUNDS OF SULPHUR WITH CHLORINE

The three following chlorides of sulphur exist ; they are all prepared by direct union of sulphur and chlorine :—



The first of these is a clear yellow liquid ; its vapour attacks the eyes ; it is an excellent solvent for sulphur, and appears to be the most stable of the three. SCl_2 has apparently only been obtained in double compounds at present (Ruff and Fiseher).

PART III.—INORGANIC CHEMISTRY (concluded)

THE METALLIC ELEMENTS

CHAPTER I

CLASSIFICATION

Distinctions between Metals and Non-Metals—Occurrence of Metals in Nature—General Remarks on the Preparation of Metals and their Compounds.

WE have already divided the elements into two principal classes, positive and negative, and have seen that this division roughly coincides with the more familiar distinction between **metals** and **non-metals**. This distinction was based mainly upon obvious physical features. Like all natural distinctions, it is sufficiently clear and definite between typical members of each class, but becomes somewhat indistinct and uncertain when we examine members not far removed from the border line. This will be illustrated if we briefly compare the two classes in regard to certain features which have at different times been considered characteristic.

State of aggregation. — Of the eighty elements named in the table (page 87), twenty (with arsenic) are non-metals. Of these ten are gases, and one is a liquid. Of the sixty metals only one is a liquid, and all the others are solid, many of them with high melting-points, but varying from platinum ($1,710^{\circ}$) to mercury (-40°). Thus,

at first sight, one would associate the solid state and the property of infusibility with a metal. Yet we find three undoubted non-metals—carbon, boron, and silicon—among the most infusible elements known, and metals, such as sodium and potassium, which melt more easily than sulphur.

Specific gravity.—As a general rule, metals are heavy and non-metals light, but the metals vary greatly in specific gravity, from platinum (21·5) to lithium (0·59); and iodine (5) is considerably heavier than magnesium (1·7) or aluminium (2·7).

Lustre.—The surface of a metal, when clean and smooth, is characterised by this property; but iodine and graphite might easily pass for metals if we were guided by this feature alone.

Malleability and ductility.—These two closely allied properties belong especially to metals, yet bismuth and antimony are brittle, like sulphur, and cannot be rolled, hammered, or drawn, without breaking.

Examples like these warn us not to look to any physical feature for an infallible indication of the character of an element. As already stated (page 17), the surest single guide is found in the character of the oxide which the element forms: If the oxide is base-forming, we place the element in the positive or metallic class; if the oxide is acid-forming the element is a negative or non-metallic one. Elements, like chromium and manganese, which form oxides of both kinds, are included among metals, but the element arsenic, which forms *only* acid-forming oxides, should really be placed with the non-metals, and in modern textbooks this plan is generally adopted. In this book it is retained in Part III. because from the point of view of the student, for whom the book is specially intended, arsenic is per-

haps more closely associated with antimony than with phosphorus.

Some metals—gold, platinum, bismuth, copper, silver—are found native in the earth's crust, but most occur as oxides, sulphides, carbonates, silicates, or chlorides. A native compound from which a metal can be profitably extracted is called an *ore*. The first step, in order to obtain the metal from the ore (after purifying the latter by mechanical means, washing, etc.), is to “roast” it—i.e. to heat it to a red heat with free access of air. This roasting drives off water, carbon dioxide, arsenic, sulphur, etc., and usually leaves the ore as oxide.



The reduction to the metallic state is usually effected by heating with carbon.



The oxides of two metals—silver and mercury—are reduced by heat alone. On the other hand, the oxides of two metals cannot be reduced even by heating with carbon; these are magnesium oxide and aluminium oxide. In such cases the oxide is converted into chloride and the latter decomposed by sodium.



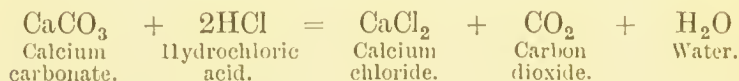
Oxides can be prepared (1) by heating the metal in air; thus, zinc oxide, tin oxide, magnesium oxide, lead oxide, etc., can be formed. (2) By heating (a) the hydroxide, which loses water and

leaves the oxide ; or (b) the carbonate which loses carbon dioxide and leaves the oxide of the metal ; or (c) the nitrate, which gives off oxides of nitrogen and leaves the oxide.

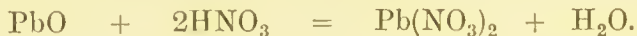
Hydrates or hydroxides, being generally insoluble, are usually obtained by precipitating a solution of a salt with ammonium hydrate or potassium hydroxide in aqueous solution. Potassium hydroxide itself, being soluble, cannot be prepared in this way. Its preparation is described on page 264.

Sulphides can be obtained (1) by fusing the metal with sulphur ; (2) by reducing the sulphate of the metal by heating it with carbon ; (3) by passing hydrogen sulphide (H_2S) through a solution of the metal (page 253).

Salts.—1. In most cases a salt can be prepared by dissolving the carbonate of the metal in the proper acid, filtering or decanting the solution, and evaporating to the point of crystallisation ; thus, to obtain calcium *chloride*, dissolve calcium carbonate in *hydrochloric acid*, decant the clear fluid, and evaporate.



2. The oxide, instead of the carbonate, may be dissolved in the required acid ; lead nitrate may, for instance, be prepared from litharge in this way.



3. The metal itself may be dissolved in the acid with evolution of hydrogen, sulphur dioxide, or oxides of nitrogen (*see* page 74), and formation of the required salt.

The above method fails *when the salt is insoluble* ; the salt is then prepared by precipitation ; thus, lead

sulphate is formed by adding dilute sulphuric acid to a solution of lead nitrate, when the sulphate falls as a white precipitate, which can be filtered off, washed, and dried.

All nitrates and chlorates are soluble in water; bismuth nitrate does not usually give a clear solution unless a little free nitric acid is added to the water.

All chlorides are soluble in water except silver, mercurous, cuprous, and lead chlorides; lead chloride easily dissolves in *hot* water.

All sulphates are soluble in water except lead, barium, strontium, and calcium sulphates (the latter is slightly soluble).

Most carbonates and phosphates (except those of sodium, potassium, and ammonium) are insoluble in water, and can be prepared by precipitating the solutions of the respective chlorides or nitrates with ammonium or sodium carbonate or phosphate. The soluble salts of sodium potassium and ammonium may be obtained by special methods described hereafter.

CHAPTER II

POTASSIUM—SODIUM—LITHIUM

Potassium: Natural Compounds of Potassium—Preparation and Properties of the Metal Potassium—Potassium Salts—Tests for Potassium. Sodium: Natural Compounds of Sodium—Preparation and Properties of the Metal Sodium—Sodium Salts—Test for Sodium. Lithium: Natural Compounds of Lithium—Preparation and Properties of the Metal Lithium—Lithium Salts—Test for Lithium.

POTASSIUM

Symbol, K ; monad ; atomic weight, 39.

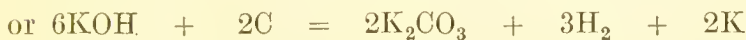
Natural compounds of potassium.—

1. *Potash felspar* (a double silicate of aluminium and potassium) in granite rocks is the original source of the potassium salts. Plants possess the property of separating and assimilating the potash from rocks and soils, storing it up in their tissues in the form of potassium salts of organic acids (tartrate, citrate, malate, etc.). On burning the wood of plants these organic salts are converted by the heat into the carbonate of potassium, which in a somewhat impure condition constitutes *wood-ash* or *pearl-ash*, from which the carbonate of potassium is extracted by water. 2. *Saltpetre* or *nitre* is native nitrate of potassium (see page 266). 3. *Carnallite* is a double chloride of potassium and magnesium found in Stassfurt, in Germany. 4. *Argol* is the crude acid tartrate of potassium, or cream of tartar ($\text{KHC}_4\text{H}_4\text{O}_6$),

found as a deposit in wine casks. Acid tartrate of potassium is originally present in solution in the juice of the grape ; and when this undergoes fermentation in the preparation of wine, the grape sugar becomes converted into alcohol, the latter throwing the acid tartrate of potassium (which is insoluble in alcohol) out of solution. The acid tartrate, carrying down with it some of the colouring matter of the grape, constitutes the deposit known as argol.

Preparation of the metal potassium.—

This metal is obtained by distilling potassium carbonate with charcoal, or a mixture of finely-divided iron and charcoal with potassium hydrate (Castner's process).



It can also be obtained now by the electrolytic processes employed for the preparation of metallic sodium (page 273), but there is not such a large demand in commerce for potassium as for sodium.

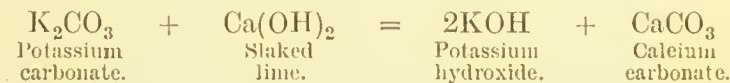
Properties of the metal.—Potassium is a metal of a white colour, and possesses a bright lustre when a piece of it is freshly cut. The cut surface rapidly tarnishes, however, owing to the action on it of the oxygen of the air, which forms a film of potassium oxide. On account of this strong affinity of potassium for oxygen, the metal has to be kept immersed in mineral naphtha, a liquid free from oxygen; otherwise, if potassium be kept exposed to the air, it is soon completely converted into potassium oxide (K_2O). The specific gravity of potassium is .875 ; it therefore floats when thrown on the surface of water ; at the same time it energetically decomposes the water. Sufficient heat is

produced to ignite the escaping hydrogen, which, from the presence in it of a little potassium, burns with a lavender-coloured flame.



On sulphuric and hydrochloric acids potassium acts with explosive violence, forming respectively potassium sulphate and chloride, and liberating the hydrogen. It also forms an explosive compound with carbon monoxide $\text{K}_2(\text{CO})_2$.

Potassium hydroxide, or caustic potash (KOH).—Prepared by boiling together potassium carbonate, slaked lime, and water, filtering from the insoluble calcium carbonate produced and evaporating.



It is usually seen in the form of hard, white sticks. The substance is very deliquescent, corrosive, and caustic, strongly alkaline, and possesses a soapy feel.

Ordinary impurities.—Chloride, sulphate, carbonate, silicate, calcium, aluminium.

Potassium hydroxide is now largely obtained by the electrolysis of potassium chloride, which behaves like potassium iodide (page 105).

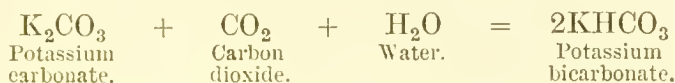
POTASSIUM SALTS

Potassium carbonate.—A pure form of this salt can be prepared by igniting cream of tartar and extracting with water. The salt is also prepared from the Stassfurt salts (page 262) by the magnesia-potash process.

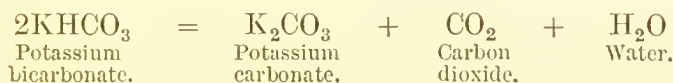
Description.—A white, hygroscopic powder, sometimes employed to abstract water from substances. Easily soluble in water. The solution is strongly alkaline.

Ordinary impurities.—As in caustic potash.

Potassium bicarbonate (KHCO_3). — Prepared by passing a stream of carbon dioxide through a cold saturated solution of potassium carbonate.



The potassium bicarbonate, being less soluble than the carbonate, crystallises out as it is formed. If boiling water be added to potassium bicarbonate, it is resolved into the carbonate, with evolution of carbon dioxide.

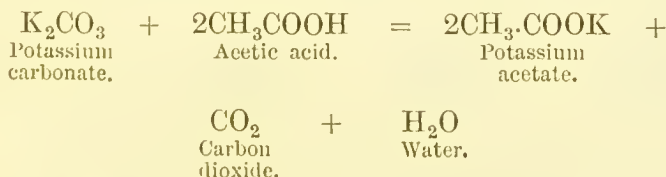


It should not, on this account, be dissolved in hot water.

Description.—Colourless crystals, soluble in water, which acquires an alkaline reaction and saline taste.

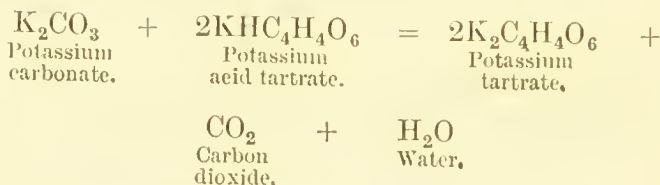
Ordinary impurities.—As in the normal carbonate.

Potassium acetate (CH_3COOK). — Prepared by neutralising acetic acid with potassium carbonate.

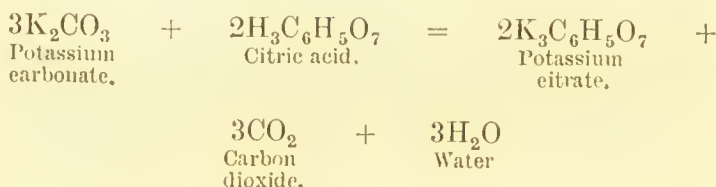


Potassium tartrate ($2\text{K}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$). — Prepared by neutralising potassium acid tartrate

(cream of tartar), dissolved in boiling water, with potassium carbonate.

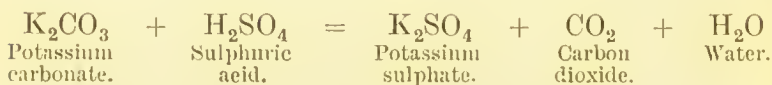


Potassium citrate ($\text{K}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$).—Prepared by neutralising a solution of citric acid with potassium carbonate.



Potassium citrate is also prepared by the action of citric acid on potassium bicarbonate.

Potassium sulphate. (K_2SO_4).—Prepared by neutralising sulphuric acid with potassium carbonate.



Also obtained as a by-product in the preparation of nitric acid from potassium nitrate and sulphuric acid.

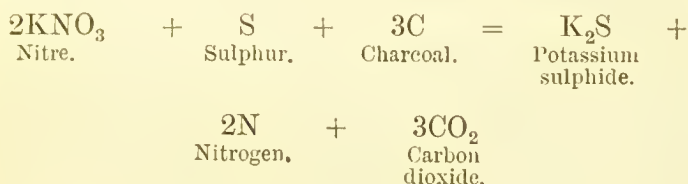


Description.—Colourless crystals, soluble in water, which remains neutral.

Ordinary impurities.—Chlorides, nitrates, metals.

Potassium nitrate (KNO_3).—Found in nature

as *nitre* or *saltpetre*. It may be prepared by neutralising nitric acid with potassium carbonate. This salt is largely employed in the manufacture of gunpowder, which is a mixture of chareoal, sulphur, and nitre; when the gunpowder is fired, the oxygen of the nitre converts the chareoal into the two gaseous oxides of carbon, carbon monoxide and dioxide, the nitrogen of the nitre is set free, and the sulphur unites with the potassium of the nitre to form potassium sulphide, which, blown into the air in minute partieles, constitutes the smoke. This may be roughly represented by the equation :



The explosive violenee is due to the sudden expansion of the large volume of the heated gases produced. The temperature produced is very high—2200°.

Description.—Clear, colourless, crystals, soluble in water, which remains neutral.

Ordinary impurities.—Chloride, sulphate, sodium, calcium, and magnesium.

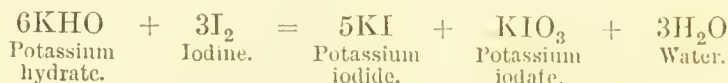
Potassium nitrite (KNO_2).—If potassium nitrate be heated to redness for some time, it loses one-third of its oxygen, and potassium nitrite is formed.

Potassium chloride (KCl) occurs in nature as *carnallite*; it can be prepared by neutralising hydrochloric acid with potassium carbonate.

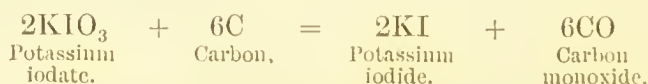
Potassium iodide (KI).—This important salt is prepared :—

1. By saturating a hot solution of caustic potash

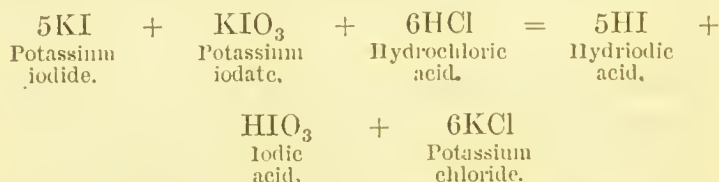
with iodine, by which means potassium iodide and iodate are obtained in solution.



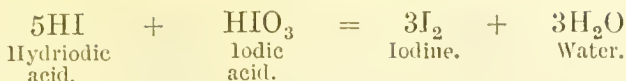
2. The solution is then evaporated to dryness, and the residue mixed with charcoal and heated, so as to convert the iodate into iodide; the carbon abstracting the oxygen from the iodate, and so reducing it to the iodide.



3. The melted mass, on cooling, is boiled with water, the solution of potassium iodide is filtered from excess of charcoal, evaporated to a low bulk, and set aside to crystallise. It is very important that the iodate of potassium should be completely converted into iodide, as any acid possesses the property of liberating iodine from a mixture of the two salts; and since iodide of potassium is a valuable drug, frequently administered in medicine, if it contained iodate the hydrochloric acid of the gastric juice would liberate iodine from the two salts within the stomach, and so the iodine might be set free in injurious quantities. The hydrochloric acid of the gastric juice would first liberate from the iodide and iodate hydriodic and iodic acids respectively.



These two acids would then by their action on one another produce free iodine and water.



To test whether a sample of potassium iodide is free from the iodate we therefore proceed as follows: Dissolve a few crystals in water, add a few drops of starch solution, and then a little acetic acid. If a blue colour appears we know that iodine has been liberated, and infer that *both* iodide and iodate were present in the sample.

Description.—White, cubical crystals, soluble in water, which should remain neutral.

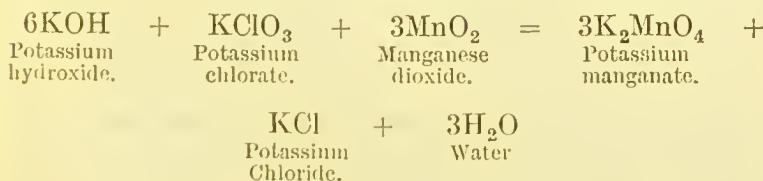
Ordinary impurities.—Chloride, bromide, iodate, carbonate, sulphate; metals.

Potassium bromide (KBr).—This salt is prepared in a manner similar to the iodide, with the substitution of bromine for iodine. It may contain potassium bromate, and in that case *bromine* will be set free, if the sample be tested as above, instead of iodine. Bromine only gives a yellow colour to starch solution.

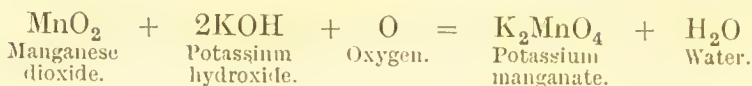
Description.—Closely resembles the iodide.

Ordinary impurities.—Chloride, iodide, bromate, carbonate, sulphate.

Potassium manganate (K_2MnO_4).—Prepared by fusing together in a crucible caustic potash, potassium chlorate and manganese dioxide, and extracting the mass with *cold* water, when a green-coloured solution of potassium manganate is obtained.

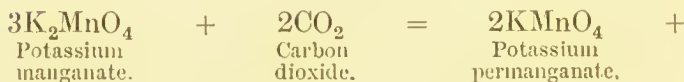
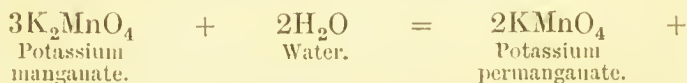


On the large scale the chlorate of potash is omitted, and the oxygen obtained directly from the air.



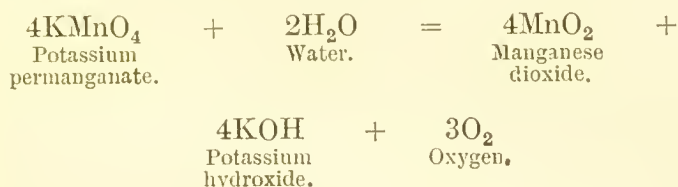
This solution of potassium manganate is used as a disinfectant. It acts partly as a germicide, and partly by the readiness with which it oxidises organic substances. It is not employed so much as the permanganate, which is a better and more powerful disinfectant.

Potassium permanganate (KMnO_4).—This salt is also known as the *red manganate of potash*. It is obtained from the manganate by the abstraction of one-half of the potassium, which can be effected either by boiling the solution of the green manganate or by passing a stream of carbon dioxide or chlorine through it. One-half of the potassium is removed respectively as potassium hydrate, carbonate or chloride, some manganese dioxide being precipitated.



By evaporating the deep-red solution to a low bulk and allowing it to cool, potassium permanganate separates in long, dark-red, almost black, needles, with somewhat of a metallic lustre. Potassium permanganate is one of the most powerful oxidising agents known, and is also a powerful disinfectant.

As a disinfectant it acts in a manner similar to the manganate, partly by being a powerful germicide, and partly by the readiness with which it oxidises organic substances. When it is being so employed, the red solution loses its colour, a brown deposit of manganese dioxide being produced. The splitting up of potassium permanganate when employed as a disinfectant is shown in the following equation :—



On account of the staining that would result from the deposition of the manganese dioxide, a solution of potassium permanganate should never be employed in the disinfection of linen or of articles of clothing. A solution of the corresponding sodium salts is very largely employed as a cheap disinfectant under the name of *Condy's fluid*.

When employed in volumetric analysis (page 599), the solutions are acidulated with sulphuric acid, which combines with the manganous oxide and so prevents the deposition of the brown deposit.

Ordinary impurities.—These are mainly important in so far as they affect the oxidising value of the substance. The B.P. requires that 1 gm. of salt should require for titration (page 599) 31·2 c.c. of normal oxalic acid. (This is equivalent to 98·6 per cent. of KMnO_4 .)

Sulphurated potash.—This preparation, which is a mixture of various potassium sulphides and potassium sulphate (K_2SO_4), is obtained by fusing together potassium carbonate and sulphur. It is an unstable preparation and was formerly known as

liver of sulphur. The colour of the solid is somewhat liver-brown when fresh. Potassium carbonate is a common impurity.

Potassium chlorate. (See page 183.)

Potassium cyanide, cyanate, ferrocyanide, and ferricyanide.—These salts are described in the Organic Chemistry Section, Chapter IX.

Potassium bichromate.—This salt is described in connection with chromium (page 355).

Tests for Potassium

1. If a potassium salt, or a solution of a potassium salt, be introduced on a loop of platinum wire into a Bunsen flame, a characteristic lavender tint will be imparted to the flame. If a sodium salt be also present, the yellow colour imparted by the sodium to the flame will entirely mask the lavender tint produced by the potassium salt; but if such a flame be viewed through a piece of dark-blue glass, the yellow sodium rays will be absorbed by the blue of the glass, while the lavender-coloured rays produced by the potassium salt will pass through the glass unchanged.

2. If a solution of a potassium salt contained in a watch-glass be acidulated with hydrochloric acid, a few drops of chloro-platinic acid added, and the mixture well stirred with a glass rod, a yellow crystalline deposit of potassium chloro-platinate (K_2PtCl_6) will be formed. A similar reaction occurs with ammonium salts.

3. If to a concentrated solution of a potassium salt a strong solution of tartaric acid be added, and the mixture be then well shaken or stirred, a white granular or crystalline precipitate of potassium acid



tartrate

| will be formed.

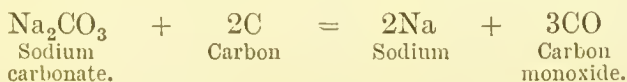


SODIUM

Symbol, Na ; monad ; atomic weight, 23.

Natural compounds of sodium.—1. Sodium chloride is the principal sodium compound occurring in nature ; in the solid form it occurs as *common salt*, or *rock-salt* ; in solution it is present in large quantities in sea-water. 2. Sodium nitrate, known as *cubic nitre* or *Chili saltpetre*, occurs in immense quantities in South America. 3. Just as potassium salts are present in land plants, and leave the carbonate when the plants are burnt, so sodium salts are present in sea-weeds, and are left as sodium carbonate when sea-weeds are burnt (*see* page 190). 4. *Cryolite* is a double aluminium and sodium fluoride ($\text{AlF}_3, 3\text{NaF}$).

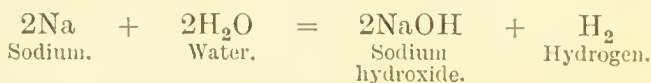
Preparation of the metal sodium.—This metal is prepared by a process similar to that employed in the preparation of potassium, viz. by distilling sodium carbonate with charcoal, or a mixture of finely-divided iron and charcoal with sodium hydrate.



Most of the metallic sodium at the present time is obtained by decomposing, by means of a powerful current of electricity, melted sodium hydrate at a temperature of 300° , nickel electrodes being used.

Properties of the metal.—Sodium very much resembles potassium in many of its properties. It is a metal of a silver-white colour and possesses a bright lustre when freshly cut, the cut surface rapidly tarnishing, however, owing to its uniting with the oxygen of the air to form a film of sodium oxide ; it is on account of this powerful affinity of sodium for oxygen that the metal has to be kept immersed

in mineral naphtha, a liquid free from oxygen, as otherwise, if kept exposed to the air, it would become completely converted into sodium oxide (Na_2O). Sodium has a specific gravity of .973, and therefore floats when thrown on water, at the same time decomposing the water energetically, forming sodium hydroxide, and liberating one-half of the hydrogen of the water.



There is not so much heat generated by the action of sodium on water as by potassium on water, and therefore, during the action of sodium on water the escaping hydrogen is not ignited; but if the movements of the sodium on the surface of the water be restrained, as, for instance, by throwing a piece of sodium on to wet blotting-paper, when it remains fixed in one spot, then the heat, being concentrated at this one spot, is sufficiently intense to ignite the escaping hydrogen. Large quantities of sodium are used for preparing sodium cyanide (for extracting gold) and sodium peroxide (used for bleaching).

Sodium oxide (Na_2O).—Prepared by heating sodium to 180° in the air; it forms a grey solid.

Sodium peroxide (Na_2O_2). — Prepared by heating sodium to 300° in excess of air; it is a white solid, and a most powerful oxidising agent. When dissolved in hydrochloric acid it forms a solution of salt and peroxide of hydrogen, which is much used for bleaching straw, etc.

Sodium hydrate or hydroxide (caustic soda). — Prepared by boiling a solution of sodium carbonate with solid slaked lime until the clear liquid ceases to effervesce; the liquid is then evaporated to dryness, and the dry residue heated till the hydrate

begins to volatilise, when it is poured into moulds and cast into sticks. The reaction should be performed in an iron or silver dish. The equation is quite similar to that given under potassium hydrate.

Sodium hydroxide is now obtained on a commercial scale by the electrolysis of salt solution. As already explained (page 105), the primary separation of the salt into the two constituents sodium and chlorine is followed by a secondary reaction, resulting in sodium hydroxide and hydrogen.

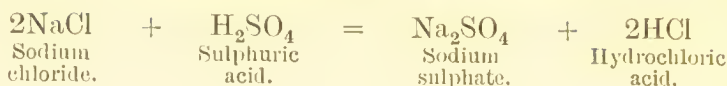


SODIUM SALTS

Sodium carbonate (Na_2CO_3). Washing-soda ($\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$).—The latter substance is manufactured on an enormous scale from common salt (NaCl). There are two methods of manufacturing sodium carbonate on a large scale, one known as the *Leblanc process*, the other and more recent one as the *ammonia-soda process*.

Leblanc process.—In this process the sodium is furnished by common salt (NaCl), and the carbonic radicle by chalk or limestone (CaCO_3). The roasting of these two substances together would be useless, since even if sodium carbonate and calcium chloride were formed, yet they could not be separated from one another, for, both being soluble in water, they would, on the addition of water, react on one another, reproducing sodium chloride and calcium carbonate. The object of the process is therefore finally to obtain an insoluble calcium compound from which sodium carbonate may be removed by solution in water. This is effected by the following steps:—

1. The sodium chloride is converted into sodium sulphate by the action of strong sulphuric acid.



2. The sodium sulphate (*salt-cake*) is then mixed with small coal and crushed limestone, and the mixture thoroughly heated in a furnace; the sodium sulphate is first reduced by the carbon of the coal to sodium sulphide.

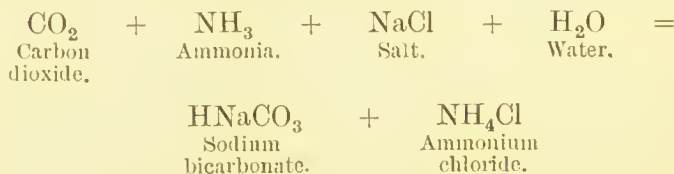


Double decomposition then takes place between the sodium sulphide and the calcium carbonate (limestone), resulting in the formation of sodium carbonate and calcium sulphide.



3. The melted mass (*black-ash*) is boiled with water in order to dissolve out the sodium carbonate, the calcium sulphide remaining insoluble; the latter is allowed to deposit; the solution of sodium carbonate is poured off and evaporated until it crystallises on cooling.

Ammonia-soda process (Solvay's process).—This consists in passing carbon dioxide into an ammoniacal solution of salt under a pressure of two atmospheres.



The bicarbonate, being less soluble than the salt, separates out as it forms; it is filtered off and

dried by steam, when it is converted into sodium carbonate.



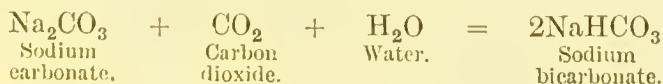
The carbon dioxide gas which is given off is again used, and the ammonia is recovered from the ammonium chloride by heating with lime.

Sodium carbonate, commonly known as *washing-soda*, is largely used to soften water for washing purposes. The water is usually first boiled, by which means the temporary hardness is got rid of (*see* page 120), and some washing-soda is then added to get rid of the permanent hardness, which is mainly due to calcium and magnesium sulphates; these compounds are converted into the insoluble calcium and magnesium carbonates by the washing-soda.

Description.—The anhydrous salt is a white powder. Washing-soda occurs in large, colourless crystals, efflorescent, and soluble in water, which becomes strongly alkaline. The solution gives an immediate red precipitate with mercuric chloride solution, and a white precipitate in the cold with magnesium sulphate solution (distinctions from the bicarbonate).

Ordinary impurities.—Chlorides, sulphates, ammonium, calcium, magnesium.

Sodium bicarbonate (NaHCO_3) is prepared by passing a stream of carbon dioxide through a saturated solution of sodium carbonate, when the bicarbonate separates out, on account of its lesser solubility.



Sodium bicarbonate, when employed in medicine,

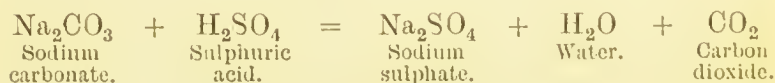
should not be dissolved in hot water, as it is converted by the heat into sodium carbonate.



Description.—White, crystalline powder, soluble in water, which becomes alkaline. The solution gives an immediate cream-coloured precipitate with solution of mercuric chloride in the cold, and no precipitate in the cold with solution of magnesium sulphate (distinctions from the normal carbonate).

Ordinary impurities.—As in the normal salt.

Sodium sulphate ($\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$).—This salt, a saline purgative, is known as *Glauber's salt*. It is prepared either by neutralising sulphuric acid with sodium carbonate, or as a by-product in the preparation of hydrochloric acid from common salt and sulphuric acid.



Description.—Clear, colourless crystals, soluble in water, which thus acquires a bitter and somewhat nauseous taste; the crystals effloresce.

Ordinary impurities.—Chlorides; other metals.

Sodium phosphate ($\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$) is prepared by partially saturating phosphoric acid with caustic soda, or, as stated in the Pharmacopœia, by the interaction of sodium carbonate and acid calcium phosphate.

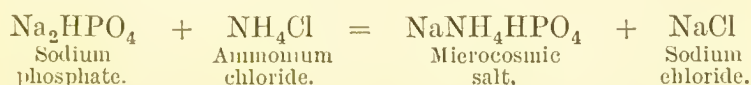


This salt, although an acid phosphate in constitution, is yet alkaline to test-paper. Another sodium phosphate (NaH_2PO_4), which can be prepared by adding to the phosphoric acid a smaller proportion of caustic soda, is acid to test-paper.

Description.—Clear, colourless crystals, soluble in water, which thus becomes alkaline. The crystals effloresce in dry air.

Ordinary impurities.—Chlorides, sulphates, carbonates; potassium, ammonium.

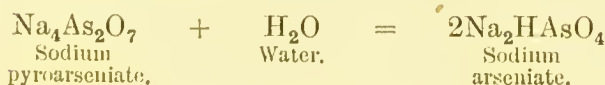
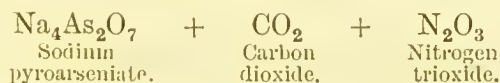
Sodium ammonium hydrogen phosphate, or **microcosmic salt** ($\text{NaNH}_4\text{HPO}_4 + 4\text{H}_2\text{O}$), is prepared by mixing boiling solutions of sodium phosphate and ammonium chloride.



It is used in blowpipe tests, as it yields, when heated, a transparent bead of sodium metaphosphate.



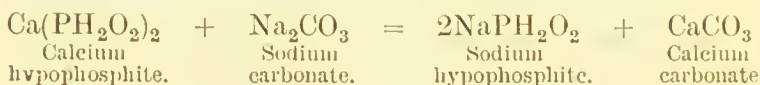
Sodium arseniate (Na_2HAsO_4) is prepared by fusing together arsenious oxide (white arsenic), sodium carbonate, and sodium nitrate, and dissolving the mass in water.



Description.—A white powder, soluble in water, which becomes alkaline.

Ordinary impurities.—Chlorides, nitrates, carbonates, sulphates; other metals.

Sodium hypophosphite ($\text{NaPH}_2\text{O}_2 + \text{H}_2\text{O}$) is prepared either by boiling phosphorus with solution of caustic soda (*see* page 231), or by decomposing a solution of calcium hypophosphite with sodium carbonate, when calcium carbonate is precipitated and sodium hypophosphite remains in solution.

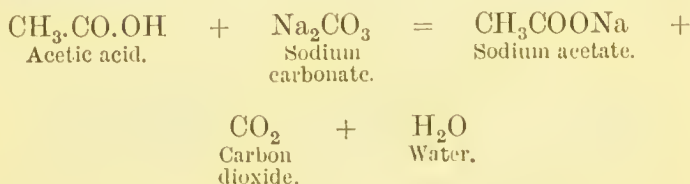


Description.—Small, white tablets, soluble in water, which then tastes bitter and nauseous.

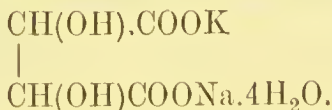
Ordinary impurities.—Carbonate, phosphate, chloride, sulphate; other metals.

Sodium iodide (NaI) and **sodium bromide** (NaBr).—These salts are prepared in ways similar to the corresponding potassium salts, which they closely resemble in appearance and general character. In the preparations caustic soda is of course substituted for caustic potash (*see* pages 267, 269).

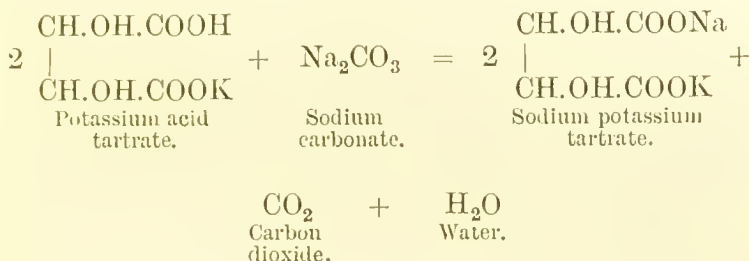
Sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) is prepared by neutralising acetic acid with sodium carbonate.



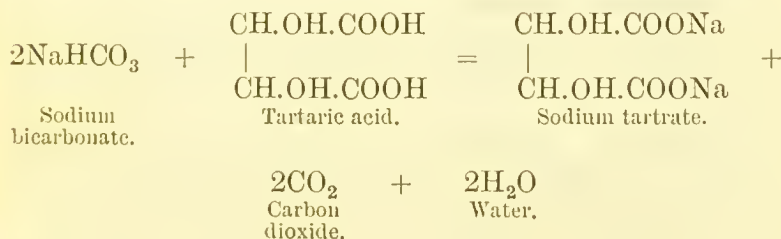
Sodium potassium tartrate



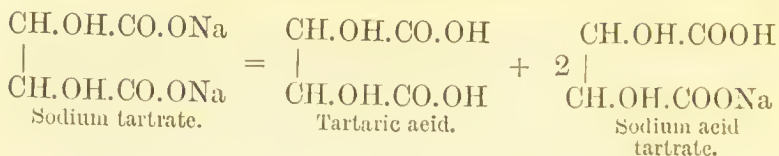
—This salt, which is used as a saline purgative, is known as *Rochelle salt*; it is prepared by neutralising a hot solution of potassium acid tartrate (cream of tartar) with sodium carbonate.



This salt constitutes the main ingredient of a *Seidlitz powder*, the blue packet of which contains a mixture of Rochelle salt and sodium bicarbonate, whilst the white packet contains tartaric acid; the contents of the blue packet are first dissolved in water, and then the contents of the white packet added; the sodium bicarbonate is neutralised by the tartaric acid, with formation of sodium tartrate and copious effervescence of carbon dioxide gas.



But as the white packet contains a slight excess of tartaric acid over and above what is required to neutralise the bicarbonate, this slight excess of acid converts a small portion of the sodium tartrate into the acid tartrate, which then gives an agreeable acidity to the draught.



So that when the contents of the two packets constituting the "scidlitz powder" are mixed in water, three salts, all of them saline purgatives, are contained in the draught, viz. sodium potassium tartrate (Rochelle salt), sodium tartrate, and sodium acid tartrate.

Sodium citro-tartrate. — This effervescing preparation, known as the *effervescing citro-tartrate of soda*, is prepared by mixing together in the solid state, sodium bicarbonate, citric acid, tartaric acid, and sugar, and then carefully heating the mass until it becomes granular. When the granules are dissolved in water, effervescence takes place, with the production of sodium citro-tartrate.

Sodium hypochlorite. (See page 182.)

Sodium hypobromite. (See page 189.)

Sodium thiosulphate or **hyposulphite.**
(See page 254.)

Sodium borate. (See page 219.)

Sodium chloride is purified common salt.

Ordinary impurities.—Sulphates, calcium, magnesium.

Sodium nitrite is prepared by fusing the nitrate with lead, or otherwise reducing it.



It is a cream-coloured deliquescent powder, but is also met with in the form of sticks. It should respond to the general tests for nitrites (see page 159).

Ordinary impurities.—Chlorides, sulphates, lead.

Sodium sulphite is prepared by neutralising solution of sulphur dioxide with sodium carbonate.

The salt occurs as colourless, efflorescent crystals ($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$), and also as a white anhydrous powder (Na_2SO_3).

Ordinary impurities.—Thiosulphate, sulphate; other metals.

Test for Sodium

If a fragment of a sodium salt, or some solution of a sodium salt, be introduced, on a loop of platinum wire, into a Bunsen flame, an intense yellow colour will be communicated to the flame; this test will be rendered all the more trustworthy by observing the appearance of the skin of the hand when seen by the yellow-coloured sodium flame. The skin assumes a somewhat ghastly hue.

LITHIUM

Symbol, Li; monad; atomic weight, 7.

Natural compounds of lithium.—Lithium occurs in the minerals *lepidolite* and *petalite*, and is also found in minute quantities in numerous mineral springs.

Preparation and properties of the metal lithium.—Lithium can be prepared by electrolysis of its fused chloride; the metal depositing on the negative pole and chlorine being liberated at the positive pole. Lithium is the lightest solid known (specific gravity, $\cdot 59$); it is a silver-white metal, harder than potassium or sodium, but oxidising less easily than those metals; its cut surface, however, soon tarnishes from absorption of oxygen and formation of lithium oxide; it is therefore kept in mineral naphtha. Like potassium and sodium, it decomposes water when thrown upon it, with the formation of lithium hydroxide and hydrogen, but the escaping hydrogen is not inflamed.

LITHIUM SALTS

Lithium carbonate (Li_2CO_3) is prepared from *lepidolite*, a double fluoride of potassium and lithium with silicate of aluminium, by decomposing it with sulphuric acid to form the three soluble sulphates of potassium, lithium, and aluminium, adding ammonia to precipitate the aluminium, filtering, evaporating to dryness, igniting the residue to expel ammonium salts, dissolving the potassium and lithium sulphates in a small quantity of water, and adding potassium carbonate to precipitate the carbonate of lithium.

Description.—A white, more or less crystalline powder, not very easily soluble in water, which it renders alkaline.

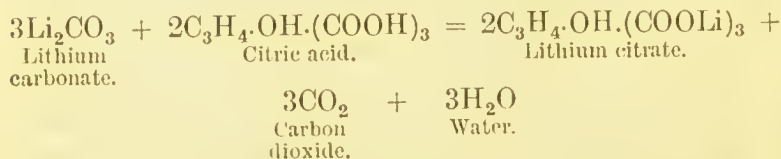
Ordinary impurities.—Sulphates, chlorides; calcium and other metals.

Lithium bicarbonate (LiHCO_3) is prepared by suspending lithium carbonate in water, and passing carbon dioxide gas, when the bicarbonate is formed and dissolves in the water.



This is the salt that is present in lithia water (*Liquor lithiæ effervescens*).

Lithium citrate is prepared by neutralising a solution of citric acid with lithium carbonate.

*Test for Lithium*

Volatile lithium salts impart a magnificent crimson colour to the Bunsen flame.

CHAPTER III

CALCIUM—BARIUM—STRONTIUM

Calcium : Natural Compounds of Calcium—Preparation of Calcium—Mortars and Cements—Calcium Salts—Tests for Calcium. Barium : Natural Compounds of Barium—Preparation of Barium—Barium Salts—Tests for Barium. Strontium : Tests.

CALCIUM

Symbol, Ca ; dyad ; atomic weight, 40 ; specific gravity, 1.85.

Natural compounds of calcium.—1. The chief calcium compound found in nature is the carbonate, which occurs in a variety of forms. In a pure crystalline form it occurs as *Iceland spar* and *calc spar* ; in less pure forms it constitutes *marble*, *chalk*, *limestone*, *oolite*, and *coral* ; the shells of mollusca and the egg-shells of birds consist mainly of calcium carbonate ; *stalactites* consist of a porous form of calcium carbonate, produced by the evaporation of hard water containing the calcium bicarbonate in solution ; they are found hanging from the roofs of limestone caves. 2. Calcium sulphate occurs in nature as *alabaster*, used as an ornamental stone ; as *selenite*, which is found in transparent plates, and is used for optical purposes ; and as *gypsum*, a form of calcium sulphate containing water of crystallisation ($\text{CaSO}_4, 2\text{H}_2\text{O}$). By heating gypsum for some time at 130° to 140° the water of crystallisation is partly expelled, and commercial

plaster of Paris is obtained; this, if mixed with sufficient water to form a paste, sets to a solid in a short time, due to the plaster of Paris (CaSO_4) uniting with the water to form gypsum ($\text{CaSO}_4, 2\text{H}_2\text{O}$), a body in which the water is in the solid state. Plaster of Paris is largely employed in this way as a cement, and by the surgeon to form a rigid casing for fractured limbs, etc. 3. Calcium fluoride is native *fluor-spar*. 4. Calcium phosphate is the principal constituent of the minerals *apatite* and *phosphorite*. 5. Calcium silicate is a constituent of many rocks.

Preparation and properties of the metal calcium.—This interesting metal is now prepared cheaply and in quantity by the electrolysis of fused calcium chloride, the calcium being deposited upon the kathode, a copper or iron rod. It is a white metal, melting at 760° , harder than lead; it decomposes water at ordinary temperatures.

Calcium oxide, or lime (CaO), is prepared by heating limestone (calcium carbonate) until all the carbon dioxide is expelled.

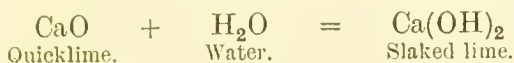


The manufacture of lime, or quicklime as it is commonly called, is carried on in specially constructed furnaces called *lime-kilns*. Fig. 31 represents such a kiln, which is constructed of fire-bricks, and is filled with pieces of limestone A. A fire is kept up at the side B, and the lime is raked out from the bottom of the kiln C as it is produced, fresh limestone being introduced at the top to supply its place.

Description.—White, hygroscopic lumps, which crumble to powder after absorption of moisture.

Ordinary impurities.—Carbonate, chloride, sulphate, phosphate, silicate; other metals.

Calcium hydrate, or slaked lime $[\text{Ca}(\text{OH})_2]$, is prepared by the addition of water to lumps of quicklime, when considerable heat is produced.



Lime-water (*liquor calcis*, B. P.) is a saturated solution of slaked lime in water, each pint containing

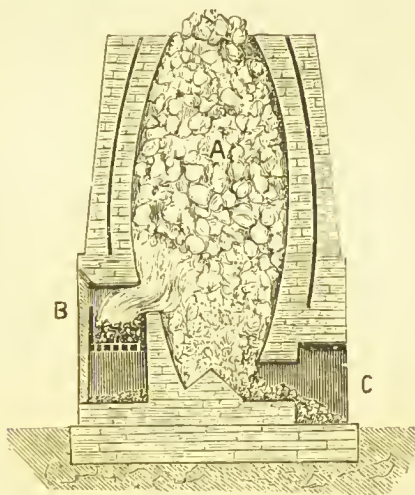
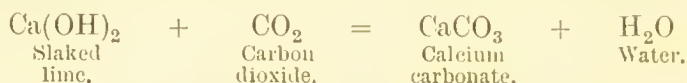


Fig. 31.—Section of lime-kiln.

about 13 grains of calcium hydrate in solution; calcium hydrate is much more soluble in an aqueous solution of sugar, and such a solution is the *saccharated lime water* (*liquor calcis saccharatus*, B. P.), which contains about 14 times as much slaked lime as ordinary lime-water. If lime-water be exposed to the air it soon diminishes in strength, owing to the absorption of carbon dioxide from the air, and consequent precipitation of calcium carbonate.

Slaked lime is largely employed in the preparation of *mortar*, which consists of slaked lime, sand, and water mixed so as to form a paste; the “setting”

of ordinary mortar is due to a slow combination of the carbon dioxide with the slaked lime.



It will be noticed that water is evolved in this reaction; this accounts for the persistent dampness of newly-built houses in which mortar is "setting." *Hydraulic mortars*, or *cements*, are preparations which, when mixed with water, solidify, and then continue to harden under water, until they assume a stone-like hardness; such are *Roman cement* and *Portland cement*, which are obtained by calcining a mixture of limestone and clay; on mixing the cement with water, compounds of lime, alumina, and silica are produced, in addition to the calcium carbonate, which set to a hard mass impervious to water. *Concrete* consists of hydraulic cement mixed with gravel or crushed pebbles.

CALCIUM SALTS

Calcium chloride ($\text{CaCl}_2 + 6\text{H}_2\text{O}$) is prepared by dissolving chalk or marble (calcium carbonate) in hydrochloric acid and evaporating the solution.

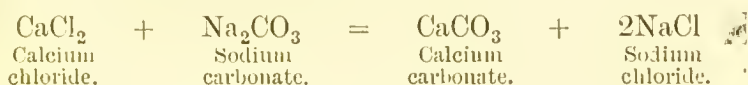


Calcium chloride, when heated to 200° , loses 4 molecules of water of crystallisation, forming a porous mass known as "fused chloride of calcium." This is one of the most hygroscopic bodies known; if exposed to the air for a short time it becomes liquid, owing to its absorbing sufficient water from the air to dissolve in; on account of its hygroscopic properties it is frequently employed to dry gases.

Description.—Colourless, deliquescent crystals, easily soluble in water, the temperature of which is lowered by the act of solution.

Ordinary impurities.—Magnesium, iron, aluminium.

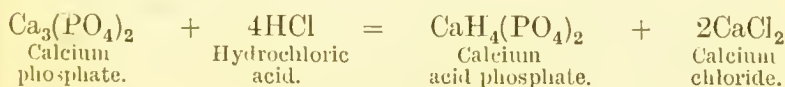
Calcium carbonate (CaCO_3).—This compound, as previously mentioned, occurs native in several forms. As *precipitated carbonate of lime*, it is prepared by precipitating a solution of calcium chloride with a solution of sodium carbonate.



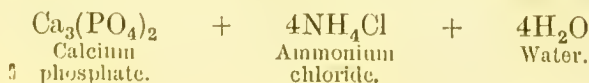
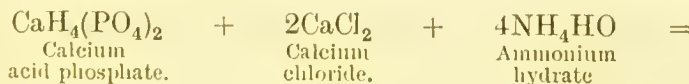
Prepared chalk is merely washed chalk that has been worked into small conical lumps and then dried ; if washed chalk be made into large rolls it constitutes *whiting*.

Ordinary impurities.—Iron, aluminium, magnesium, chloride sulphate, phosphate.

Calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$] is prepared by digesting bone-ash (impure calcium phosphate) in hydrochloric acid, by which means the insoluble calcium phosphate is converted into the soluble calcium superphosphate or acid phosphate and calcium chloride.



This acid solution is then filtered from insoluble matter, and ammonia added to precipitate the pure calcium phosphate.



Description.—A light, white powder.

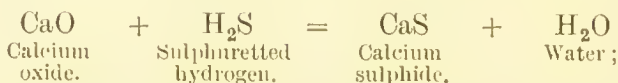
Ordinary impurities.—Carbonate, chloride, silicate; other metals.

Calcium hypophosphite. (*See* page 231.)

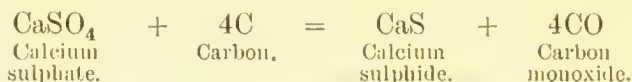
Description.—A white crystalline salt, with a pearly lustre, and a bitter nauseous taste (B.P.).

Ordinary impurities.—Chloride, sulphate, phosphate, phosphite; other metals.

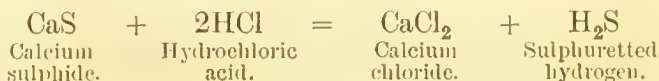
Calcium sulphide (CaS) is prepared by heating lime in a stream of sulphuretted hydrogen gas—



or by heating a mixture of calcium sulphate and charcoal, the latter reducing the sulphate to sulphide.



If calcium sulphide be exposed to light, it is afterwards for some time phosphorescent in the dark. It is the chief constituent of *Balmain's luminous paint*. If treated with an acid, such as hydrochloric acid, sulphuretted hydrogen gas is evolved, and in this way is obtained in a very pure state, such as is required in toxicological investigations.



Chlorinated lime or bleaching powder (*see* page 180.)

Description.—White powder, with characteristic chlorous smell.

Ordinary impurities.—As in slaked lime.

Tests for Calcium

1. Ammonium oxalate gives, with a solution of a calcium salt, a white precipitate of calcium oxalate insoluble in acetic acid, but soluble in hydrochloric acid. If this precipitate be strongly heated on platinum foil, and the residue (calcium oxide) laid upon moist red litmus paper, the contact will cause the paper to turn blue.

2. If a calcium salt be introduced into the Bunsen flame, on a piece of platinum wire previously moistened with hydrochloric acid, an orange-red colour is communicated to the flame.

BARIUM

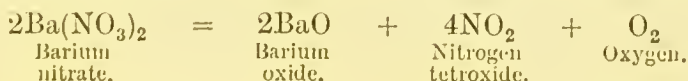
Symbol, Ba ; dyad ; atomic weight, 137.4.

The salts of barium have a high specific gravity ; hence the derivation of the name from βαρύς, *heavy*. They are poisonous ; the antidote is sodium or magnesium sulphate.

Natural compounds of barium — 1. *Witherite* is the native carbonate of barium. 2. *Heavy spar* is the native sulphate of barium.

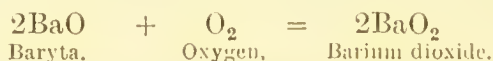
Preparation and properties of the metal barium. — Barium has been prepared from an amalgam obtained, in the electrolysis of barium chloride, at a mercury kathode (Guntz). It is a white metal, specific gravity about 3.8, and melts between 800° and 900°. Like calcium, it decomposes water at ordinary temperatures.

Barium oxide or baryta (BaO).—This oxide is most conveniently prepared by heating the nitrate.



When water is added to barium oxide, evolution of heat takes place, and *barium hydroxide* or *slaked baryta* $[\text{Ba}(\text{OH})_2]$ is produced, the reaction being similar to that which occurs during the slaking of lime. Barium forms a crystalline hydrate $[\text{Ba}(\text{OH})_2 + 8\text{H}_2\text{O}]$ which is much more soluble in water than calcium hydrate; its solution is known as *baryta water*, and, like lime-water, if exposed to the air it absorbs carbon dioxide, producing a white deposit of barium carbonate.

Barium dioxide, or **barium peroxide** (BaO_2) .—This oxide is prepared by heating baryta to a dull-red heat in a stream of air or oxygen.



If the higher oxide be further heated it is converted into the lower oxide, with evolution of oxygen; in this way pure oxygen may be obtained from the air. Barium dioxide is also employed in the preparation of hydrogen dioxide (page 125).

BARIUM SALTS

Barium nitrate $[\text{Ba}(\text{NO}_3)_2]$ is prepared either by dissolving the carbonate in nitric acid, or by reducing the sulphate to sulphide by heating with charcoal, and then dissolving the sulphide in nitric acid.

Barium chloride $(\text{BaCl}_2 + 2\text{H}_2\text{O})$ is prepared by processes similar to those used for obtaining the nitrate, with the substitution of hydrochloric for nitric acid.

Tests for Barium

1. Barium salts give, with calcium sulphate solution, an immediate white precipitate of barium sulphate, which is insoluble in either hydrochloric or nitric acids.

2. Solution of potassium chromate gives a yellow precipitate of barium chromate with barium salts; this precipitate is insoluble in acetic acid, but is soluble in either hydrochloric or nitric acids.

3. If a barium salt be introduced into the Bunsen flame, on a piece of platinum wire previously moistened with hydrochloric acid, a delicate green colour is communicated to the flame.

STRONTIUM

Symbol, Sr ; dyad ; atomic weight, 87.6.

Strontium occurs in nature as the carbonate *strontianite*, and as the sulphate *celestine*. The salts of strontium are not of any medical importance; they are prepared by processes similar to those employed in the manufacture of the calcium and barium salts.

Strontium hydrate is used in sugar refining.

Tests for Strontium

1. Strontium salts, when introduced into the Bunsen flame on a piece of platinum wire previously moistened with hydrochloric acid, communicate a beautiful crimson colour to the flame. The nitrate and chlorate are on this account largely employed by fireworks manufacturers.

2. The addition of ammonium sulphate solution to an aqueous solution of a strontium salt produces a white precipitate of strontium sulphate (SrSO_4).

CHAPTER IV

MAGNESIUM—ZINC—CADMIUM—MERCURY

Magnesium: Natural Compounds of Magnesium—Preparation and Properties of the Metal—Magnesium Salts—Test for Magnesium. Zinc: Natural Compounds of Zinc—Preparation and Properties of the Metal—Zinc Salts—Tests for Zinc. Cadmium. Mercury: Occurrence in Nature—Preparation and Properties of the Metal—Mercurous and Mercuric Salts—Tests for Mercury—Distinguishing Tests between Mercurous and Mercuric Salts. Points of Resemblance between the Metals in this Group.

MAGNESIUM

Symbol, Mg; dyad; atomic weight, 24.3; specific gravity, 1.75.

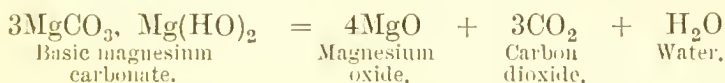
Natural compounds of magnesium.—

1. The carbonate occurs in nature in a fairly pure form as *magnesite* (MgCO_3), and as a double carbonate of magnesium and calcium in *dolomite*. 2. Magnesium sulphate is found in certain mineral-spring waters; in Epsom spring waters, in England; in Friedrichshall water, in Germany; and in Hunyadi János water, in Hungary. 3. Various compounds of magnesium and silica occur in nature; *talc* is magnesium silicate; *meerschaum* is a hydrated magnesium silicate; *asbestos* is a double silicate of magnesium and calcium.

Preparation and properties of the metal magnesium.—Magnesium can be prepared by heat-

ing in a crucible a mixture of magnesium chloride and the metal sodium, when the latter abstracts the chlorine, forming sodium chloride, and the metal magnesium sinks to the bottom of the crucible. It has more recently been made by the electrolysis of fused carnallite (MgCl_2 , KCl , $6\text{H}_2\text{O}$). Magnesium is made into ribbon or wire for burning purposes, in order to produce the powerful light known as the *magnesium light*. When burnt, it produces a white ash of magnesium oxide, or magnesia; it melts at 633° .

Magnesium oxide or **magnesia** (MgO).—This is obtained by heating the basic magnesium carbonate.



There are two varieties of the oxide, *light magnesia* and *heavy magnesia*; they are respectively prepared by the action of heat on the light and the heavy carbonates. The old name for these preparations was “calced magnesia.”

Description.—A white, very infusible powder. Barely soluble in water, but when laid on moist red litmus paper leaves a blue mark.

Ordinary impurities.—Carbonate, chloride, sulphate; iron, aluminium, calcium.

MAGNESIUM SALTS

Magnesium sulphate ($\text{MgSO}_4 + 7\text{H}_2\text{O}$), commonly known as *Epsom salts*, on account of its natural occurrence in Epsom spring waters, is prepared by dissolving the native magnesium carbonate in diluted sulphuric acid, concentrating the liquor, and allowing the salt to crystallise out.

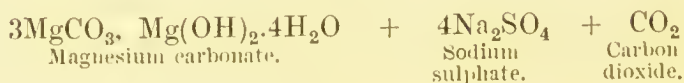
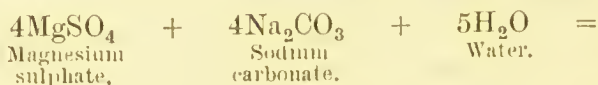


Epsom salts bear a striking resemblance in crystalline appearance to the crystals of zinc sulphate, and also in a less degree to the crystals of oxalic acid. Both these poisonous compounds have been mistaken for this popular aperient. From zinc sulphate, Epsom salts may be distinguished by its solution yielding no precipitate, either with ammonium sulphide, or with potassium ferrocyanide, whereas zinc sulphate yields a white precipitate with both reagents; from oxalic acid, Epsom salts may be distinguished by being neutral to test-paper, whereas the former is strongly acid. Oxalic acid, when heated on a knife-blade or platinum foil, leaves no residue; both zinc sulphate and magnesium sulphate leave, when heated strongly, an infusible residue of their respective oxides.

Description.—Clear, colourless crystals, soluble in water.

Ordinary impurities.—Chloride, nitrate; other metals.

Magnesium carbonate [3MgCO_3 , $\text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$].—The normal magnesium carbonate (MgCO_3) occurs native in magnesite and dolomite; the carbonate used in medicine is a basic carbonate, consisting of three molecules of the carbonate to one of the hydrate. It is prepared by mixing solutions of magnesium sulphate and sodium carbonate, when it is thrown down as a white precipitate.



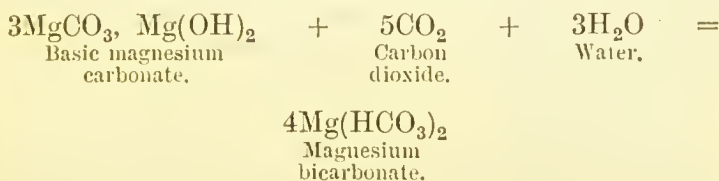
There are two forms of magnesium carbonate employed in medicine, the *light carbonate* and the

heavy carbonate. The former is obtained, as a very fine and light precipitate, by mixing somewhat diluted and cold solutions of magnesium sulphate and sodium carbonate; the latter, as a dense and more compact precipitate, is prepared by mixing strong and hot solutions of the same salts.

Description.—A white, more or less crystalline powder.

Ordinary impurities.—Chloride, sulphate; iron, aluminium, calcium.

Magnesium bicarbonate $[\text{Mg}(\text{HCO}_3)_2]$.—This soluble salt is contained in fluid magnesia (*liquor magnesiæ carbonatis*, B. P.); it is prepared by passing a stream of carbon dioxide gas through water in which magnesium carbonate is suspended.



If this solution be heated, carbon dioxide is evolved, and the magnesium carbonate is deposited.

Magnesium citrate $[\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2]$.—This salt is contained in the *liquor magnesiæ citratis*, which is prepared by dissolving the basic carbonate in solution of citric acid. “Effervescing citrate of magnesia” is a granular preparation largely used as a mild saline purgative, and effervescing when mixed with water; it consists of sodium bicarbonate, citric and tartaric acids, magnesium carbonate or sulphate, and sugar. Many specimens, however, contain no magnesium salt.

Test for Magnesium

The presence of magnesium can only be proved after the removal of the other alkaline earth metals,

viz. calcium, barium, and strontium; these metals are precipitated by ammonium carbonate *in presence of ammonium chloride*, whereas, under such conditions, magnesium is not precipitated. To test for magnesium, it is therefore necessary to add to the solution ammonium chloride and ammonium carbonate, and warm; if calcium, barium, or strontium is present, it will be precipitated, and on filtering from the precipitate, the presence of magnesium in the filtrate can be demonstrated by the addition of solution of ammonia and of sodium phosphate, when a white granular or crystalline precipitate (ammonio-magnesium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) will be thrown down. Since the metals calcium, barium, and strontium all yield precipitates with sodium phosphate, the necessity for removing them before testing for magnesium is obvious.

ZINC

Symbol, Zn; *molecule*, Zn; *dyad*; *atomic weight* 65.4; *molecular weight*, 65.4; *specific gravity* 7.15.

Natural compounds of zinc.—1. *Calamine*, the native carbonate of zinc (ZnCO_3); it is of a yellowish-white colour, from a small quantity of iron or manganese contained in it, and is used in surgery in the form of an ointment and lotion. 2. *Blende*, the native sulphide of zinc (ZnS). 3. The red oxide (ZnO); the red colour is due to manganese. 4. Zinc silicate ($\text{Zn}_2\text{SiO}_4 + \text{H}_2\text{O}$).

Preparation of the metal zinc.—The zinc ore, either calamine or blende, is first heated or roasted in the air, to convert it into the zinc oxide, which is then reduced to the metal by heating with charcoal or fine coal. Since zinc is a volatile metal, it is prepared by a process of distillation. The mix-

ture of zinc oxide and charcoal or coal is placed in tube-shaped retorts (*R*, Fig. 32) of fire clay, to the open end a conical clay pipe *a* is fitted, and to this is fixed an iron condenser *b*.

On being strongly heated, the zinc is set free by the reducing action of the carbon on the zinc oxide, and passes along the pipe in the form of vapour, which in the cooler portion of the pipe condenses to molten zinc; from time to time the iron condenser is taken away, and the melted zinc scraped out from the conical clay pipe into a ladle, until all the zinc has been distilled over. Zinc prepared in this manner is generally impure, from the presence of small quantities of arsenic, from which it can be purified by well stirring with the molten zinc some potassium nitrate; this converts the arsenic into potassium arseniate.

Granulated zinc, the form in which the metal is commonly employed in the preparation of hydrogen, is obtained by pouring melted zinc from a height into water.

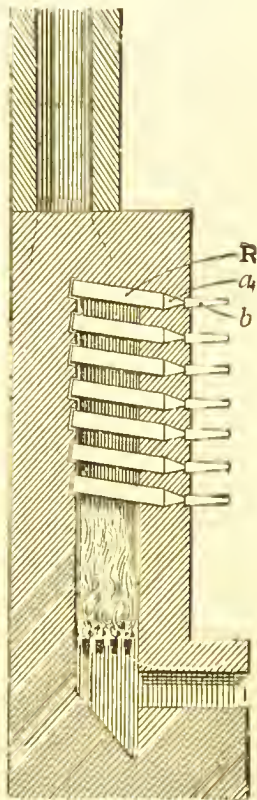


Fig. 32.—Belgian zinc furnace-section.

Properties of the metal zinc.

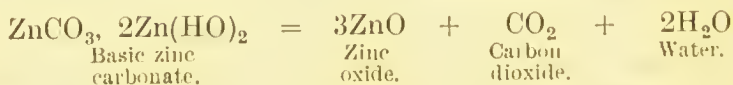
Zinc is a bluish-white hard metal; if heated to 100° — 150° it becomes soft and malleable, so that it can be rolled into thin plates; at 200° it is quite brittle, and can then be readily reduced to powder; at 419° it melts, and boils at a bright-red heat (about 940°); when strongly heated in the air it burns with

a bright, bluish flame, forming light white flocks of zinc oxide. In moist air it oxidises, becoming covered with a very thin film of zinc oxide, which, however, is a very compact film, and effectually checks any further oxidation; in this respect it is very unlike the metal iron, which in moist air oxidises or rusts continuously, and so becomes in time thoroughly corroded. Zinc is employed for coating iron vessels, etc., to prevent their rusting, such coated iron being known as *galvanised iron*.

Zinc enters into the composition of some important alloys. *Brass* is an alloy of zinc and copper; *German silver* is an alloy of zinc, copper, and nickel. *Galvanised iron*, as we have seen, is prepared by dipping clean iron into molten zinc, and so coating the iron with a covering of zinc. Zinc is readily acted on by most acids; dilute sulphuric and hydrochloric acids attack it, forming respectively zinc sulphate and chloride, with evolution of hydrogen. Moderately diluted nitric acid is peculiar in its action on zinc, producing zinc nitrate and ammonia gas, the latter, however, not escaping, but being, immediately it is formed, converted by some of the nitric acid into ammonium nitrate.



Zinc oxide (ZnO) is prepared either by burning the metal zinc in air, or by heating the basic zinc carbonate.



Zinc oxide under the name of *zinc-white* is used as a paint; it possesses this advantage over white lead, that it is not blackened by sulphuretted hydro-

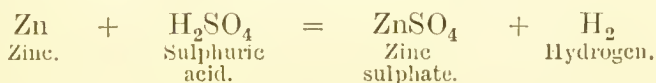
gen, whereas white-lead paint slowly blackens on account of the small quantities of sulphuretted hydrogen present in the air of towns and dwelling-houses. The covering power or "body" of zinc-white is, however, said to be not so great as that of white lead.

Description.—A soft, white powder, which turns yellow when heated, but becomes white again when cold. Moistened with solution of cobalt nitrate and heated, the oxide becomes green (*see* Test 3, page 303).

Ordinary impurities.—Carbonate, chloride, sulphate; other metals.

ZINC SALTS

Zinc sulphate ($\text{ZnSO}_4 + 7\text{H}_2\text{O}$) is prepared by the action of dilute sulphuric acid on zinc.



Description.—Zinc sulphate occurs in clear, colourless crystals, very much resembling magnesium sulphate, for which it is apt to be mistaken. For the methods of distinguishing the two salts, *see* page 296.

Zinc sulphate is occasionally termed *white vitriol*; it is an emetic.

Ordinary impurities.—Chloride; other metals.

Zinc chloride (ZnCl_2) is prepared in solution by the action of hydrochloric acid on zinc.

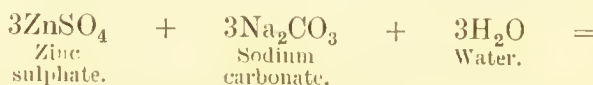


It is very poisonous; it is used as a disinfectant, under the name of "Burnett's fluid"; it coagulates albumin. When melted it dissolves metallic oxides, and is largely used in soldering with tin and lead alloys.

Description.—White, deliquescent, sticks, which have a caustic action on animal tissue.

Ordinary impurities.—Sulphate; other metals.

Zinc carbonate $[\text{ZnCO}_3, 2\text{Zn}(\text{OH})_2\text{H}_2\text{O}]$.—The normal carbonate (ZnCO_3) only occurs in nature as *calamine*. The precipitated carbonate is a basic carbonate, or double carbonate and hydrate, and is prepared by mixing solutions of zinc sulphate and sodium carbonate, when it is thrown down as a white precipitate.



Description.—A white powder. When strongly heated the salt loses carbon dioxide, and water, and is converted to the oxide.

Ordinary impurities.—Chloride, sulphate; other metals.

Zinc acetate $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2]$ is prepared by the action of acetic acid on the basic zinc carbonate.

Zinc valerianate $[\text{Zn}(\text{C}_5\text{H}_9\text{O}_2)_2 + 2\text{H}_2\text{O}]$ is prepared by mixing strong and hot solutions of zinc sulphate and sodium valerianate; on cooling, the valerianate of zinc separates out as a crystalline white substance.

Tests for Zinc

1. Ammonium sulphide gives, in neutral, or alkaline, solutions of a zinc salt, a white precipitate of zinc sulphide (ZnS). This is a characteristic reaction, as zinc sulphide is the only white sulphide capable of being precipitated.

2. Solution of ammonia gives a white precipitate

of zinc hydroxide [$\text{Zn}(\text{OH})_2$], readily soluble in excess of ammonia. From this solution in the excess of ammonia the zinc may be precipitated as the white sulphide by the addition of ammonium sulphide.

3. When heated with the blowpipe on charcoal, zinc salts leave a residue of zinc oxide which glows in the flame, turning yellow when hot and white on cooling. If this be moistened with cobalt nitrate and again made red hot, a bright green mass is obtained.

4. Potassium ferrocyanide gives a white precipitate of zinc ferrocyanide.

CADMIUM

Symbol, Cd ; *atomic weight*, 112.3 ; *specific gravity*, 8.6.

Cadmium is a tin-white metal ; it occurs as sulphide with zinc ores, and closely resembles that metal in its properties and its compounds. It is more volatile than zinc, and this property is useful in facilitating the separation of the two metals. It melts at 321.7° and boils at 778° ; it burns with a bright flame, forming a brown oxide. Its sulphide is bright yellow, and is used as a pigment (*cadmium yellow*).

MERCURY

Symbol, Hg ; *molecule*, Hg ; *dyad* ; *atomic weight*, 200 ; *molecular weight*, 200.

Natural compounds of mercury.—1. The chief natural compound of mercury is *cinnabar*, a sulphide of mercury (HgS), which is found in masses of a dark-red colour. 2. Mercury is occasionally found in the free state in small quantities.

Preparation of the metal mercury.—It is obtained from cinnabar by heating it with quick-

lime in retorts, when double decomposition first takes place between the cinnabar and the lime, resulting in the formation of mercuric oxide and calcium sulphide.



The mercuric oxide is then decomposed by the heat into mercury and oxygen, the mercury distilling over, and being condensed in a suitable receiver.

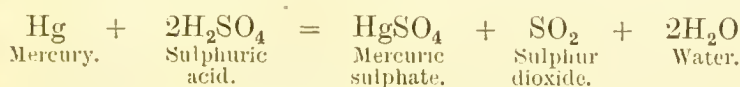
Mercury may also be obtained by roasting cinnabar in excess of air, and passing the resulting vapours of mercury and sulphur dioxide through a series of condensing chambers to condense the mercury.

The mercury of commerce is frequently contaminated with foreign metals and other matter. The presence of impurities is shown by the tendency of a globule of the sample to "tail" or assume a pear-like shape when rolled on a slightly inclined surface. An estimate of the total impurity may be made by dissolving a weighed portion of the sample in nitric acid, evaporating to dryness, igniting, and weighing the residue. Pure mercury is volatile, and should leave no residue when thus treated. Impure mercury may be purified by (*a*) redistillation with iron filings or cinnabar, or (*b*) by stirring for some time with dilute nitric acid.

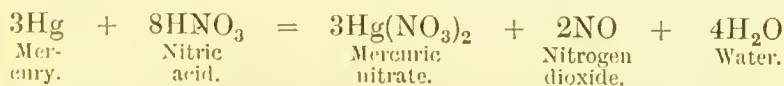
Properties of the metal mercury.—At ordinary temperatures mercury is a heavy, lustrous liquid; it is the only metal that is liquid at ordinary temperatures; it is commonly known as *quicksilver*, on account of its possessing a white colour like silver, and from its being liquid. Its specific gravity at 0° is 13·6, it solidifies at -39°, and boils at 357°; it volatilises slowly at ordinary temperatures; it remains unchanged in air at ordinary temperatures, but when heated to 300°, in contact with air, it oxidises,

forming the red oxide of mercury. It is capable of a very fine state of division if well rubbed with certain substances, and in this finely-divided state it is employed in some medicinal preparations. Those containing such finely-divided mercury are blue pill (*pilula hydrargyri*), grey powder (*hydrargyrum cum creta*), and mercury ointment (*unguentum hydrargyri*). Mercury unites with most of the metals, forming *amalgams*, the most useful of which is an amalgam of mercury and tin, which is used for silvering ordinary looking-glasses. Mercury does not unite, or amalgamate, with iron or platinum, hence it is generally stored in large iron bottles.

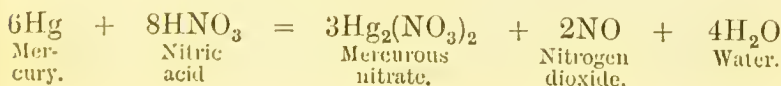
Action of acids on mercury (page 74). — Dilute sulphuric acid and hydrochloric acid have no action on mercury. Strong sulphuric acid with heat acts on mercury, forming mercuric sulphate, and evolving sulphur dioxide.



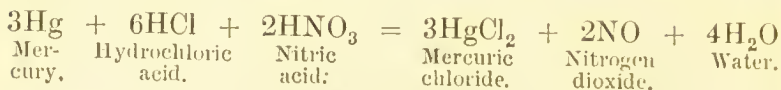
Nitric acid acts on mercury, producing different mercury salts, accordingly as strong or dilute nitric acid is employed with heat or without. Strong nitric acid with heat forms mercuric nitrate, with evolution of nitrogen dioxide.



Moderately diluted nitric acid (1 in 5) digested with mercury in the cold, forms mercurous nitrate with evolution of nitric oxide.



Aqua regia (nitro-hydrochloric acid) dissolves mercury, forming mercuric chloride, and evolving nitric oxide.



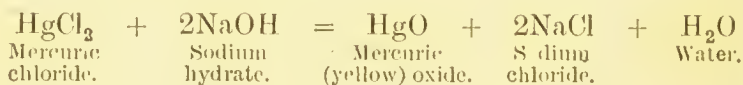
Mercuric oxide (HgO).—There are two varieties of this oxide—the *red* or crystalline variety, and the *yellow* or amorphous variety. The red mercuric oxide, commonly known as *red precipitate*, is obtained as a red crystalline powder by heating mercuric nitrate alone or mixed with metallic mercury.



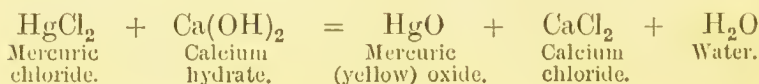
It may also be obtained by heating mercury with exposure to the air for some time at a temperature of about 350° .

Ordinary impurities.—Chloride, nitrate; arsenic, or other metals, red-lead, brick dust, or other non-volatile residue.

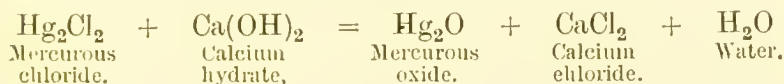
The yellow mercuric oxide is obtained as a yellow amorphous powder by precipitating a solution of mercuric chloride with any of the fixed alkalies, potash, soda, or lime.



The yellow mercuric oxide is contained in *yellow lotion* or *yellow wash* (*lotio hydrargyri flava*), in which it is made by precipitating a weak solution of mercuric chloride with lime-water.



Mercurous oxide (Hg_2O) is also known as *black oxide of mercury*; it is prepared by the action of one of the fixed alkalies, potash, soda, or lime, on a mercurous salt; it is contained in *black lotion* or *black wash* (*lotio hydrargyri nigra*), in which it is obtained as a black precipitate by shaking together calomel (mercurous chloride) and lime-water.

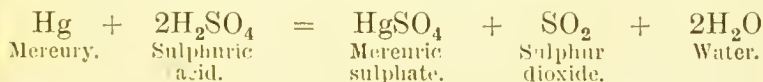


MERCURY SALTS

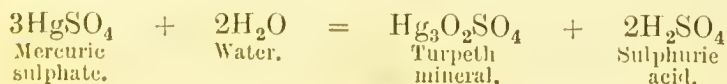
There are two classes of mercury salts, *mercuric* and *mercurous*. Although only the valency of the mercury appears to differ in the two classes, yet this difference is accompanied by many striking differences in colour, solubility, etc., as is seen in the two chlorides and the two iodides, for instance.

It will be convenient to describe the various mercuric and mercurous salts together.

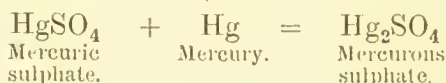
Mercuric sulphate ($\text{HgSO}_4 + \text{H}_2\text{O}$) is prepared by the action of strong sulphuric acid with heat on mercury.



Mercuric sulphate is largely used in the preparation of mercuric chloride (corrosive sublimate), and also for preparing mercurous sulphate, from which calomel is made. Mercuric sulphate is decomposed by water, with production of a yellow basic sulphate of mercury ($\text{HgSO}_4 \cdot 2\text{HgO}$), formerly employed in medicine under the name of *turpeth mineral*.



Mercurous sulphate (Hg_2SO_4).—This is prepared by well rubbing mercuric sulphate with as much mercury as it already contains.



This salt is used for the preparation of calomel; it is very apt to be contaminated with some unchanged mercuric sulphate.

Mercuric chloride (HgCl_2).—This important salt is also known as *perchloride of mercury*, *bichloride of mercury*, and *corrosive sublimate*. It is prepared by heating a mixture of mercuric sulphate and sodium chloride (common salt), a little black oxide of manganese being added to prevent the formation of mercurous chloride, and conveying the vapour of the mercuric chloride into a cool chamber, where it condenses to a white crystalline solid.



Mercuric chloride is a very poisonous substance; it is soluble in water, but if the solution is kept exposed to light it slowly decomposes, depositing mercurous chloride (calomel). A weak aqueous solution of mercuric chloride (1 part in 1,000 of water) is a powerful germicide, and is largely used in surgery as an antiseptic lotion; in using it, care should be taken not to dip articles of gold, such as rings, into it, as they would quickly become coated with metallic mercury. It coagulates albumin, forming an insoluble compound; white of egg is therefore used as an antidote in cases of poisoning by corrosive sublimate.

Description.—Heavy, colourless crystals, soluble in water, alcohol, and ether.

Ordinary impurities.—Non-volatile matter.

Mercurous chloride (Hg_2Cl_2 , or HgCl).—This largely employed mercurial preparation is also known as *calomel* and *subchloride of mercury*. It is prepared by heating a mixture of mercuric sulphate, mercury, and sodium chloride (common salt), when the calomel that is formed volatilises, and the vapour is conveyed into a cool chamber, within which it condenses to a white powder.



Calomel is apt to be contaminated with corrosive sublimate formed from the mercuric sulphate; the calomel must be freed from this impurity by thoroughly washing it with hot water, until the washings cease to show the presence of corrosive sublimate, as indicated by their no longer giving a black precipitate with ammonium sulphide. As calomel is given in fairly large doses (5 to 10 grains), it is most important that it should be thoroughly freed from the poisonous corrosive sublimate. A simple test for the detection of the latter impurity in calomel is to place some of the calomel on a clean knife-blade, moisten it with a few drops of alcohol, and allow it to remain for a few minutes, when a black spot will be produced on the blade if corrosive sublimate is present.

Another method of preparing calomel is to precipitate it from a solution of mercurous nitrate by means of hydrochloric acid.



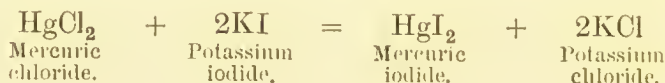
This process is not employed for the preparation of the calomel used in medicine, the sublimation process

always being used for the commercial production of calomel.

Description.—A heavy, cream-coloured powder, insoluble in water, alcohol, or ether; instantly blackened by solution of ammonia.

Ordinary impurities.—Corrosive sublimate, white precipitate; non-volatile matter.

Mercuric iodide (HgI_2), also known as the *biniodide of mercury* and the *red iodide of mercury*, is prepared by precipitating a solution of mercuric chloride with potassium iodide. It is thrown down at first as a yellow precipitate, rapidly changing to red.



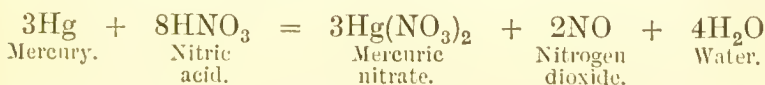
The precipitated mercuric iodide is soluble in excess either of mercuric chloride or of iodide of potassium, but especially the latter; with excess of potassium iodide it forms a soluble double iodide ($\text{HgI}_2, 2\text{KI}$), which is a very convenient and frequently employed form of administering mercury internally. This is generally done by prescribing together a suitable dose of perchloride of mercury (*liquor hydrargyri perchloridi*) with excess of potassium iodide. A weak solution of this double iodide (1 part in 2,000 or 3,000 of water) is also a powerful germicide and disinfectant, and is employed as an antiseptic lotion. *Nessler's solution* is a solution of this double iodide of mercury and potassium mixed with caustic potash. It constitutes an extremely delicate test for ammonia, and can be used for the detection of most minute quantities of ammonia in drinking waters, imparting a yellow or brownish tint to the water, according to the amount of ammonia present. This test is known as *Nessler's test*.

Description.—Red, crystalline powder, turning yellow when laid on a sheet of white paper and gently warmed over a lamp; soluble in ether (absence of mercurous iodide).

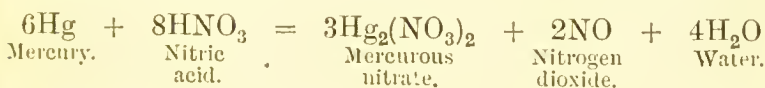
Ordinary impurities.—Non-volatile matter.

Mercurous iodide (Hg_2I_2 , or HgI), also known as the *green iodide of mercury*, is prepared by direct combination of its elements in suitable proportions—i.e. by rubbing 200 parts of mercury with 127 parts of iodine and a little alcohol, the latter being used to prevent elevation of temperature, due to the chemical action taking place; it also promotes the action of the iodine by bringing it into solution.

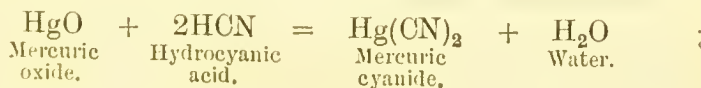
Mercuric nitrate [$\text{Hg}(\text{NO}_3)_2 + 8\text{H}_2\text{O}$] is prepared by the action of strong nitric acid with heat on the metal mercury.



Mercurous nitrate [$\text{Hg}_2(\text{NO}_3)_2 + 2\text{H}_2\text{O}$, or $\text{HgNO}_3 \cdot 2\text{H}_2\text{O}$] is prepared by the action of moderately diluted nitric acid in the cold on the metal mercury.

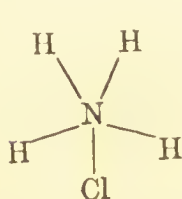


Mercuric cyanide [$\text{Hg}(\text{CN})_2$].—If red mercuric oxide is digested in dilute hydrocyanic acid, it dissolves, and mercuric cyanide is afterwards deposited in crystals.

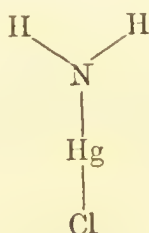


The crystals are decomposed by heat and evolve cyanogen gas, which burns, when lit, with a rose-coloured flame.

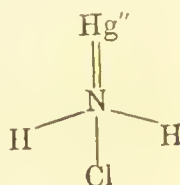
Ammoniated mercury (NH_2HgCl). — This compound, commonly known as *infusible white precipitate*, is mercuric ammonium chloride; it may consist of ammonium chloride (NH_4Cl) from which two atoms of the monad hydrogen have been displaced by one atom of the dyad mercury, or it may be a mercury compound which is half amine (page 427) and half chloride. The difference in structure of these compounds is rendered evident by inspection of their graphic formulæ.



Ammonium
chloride.

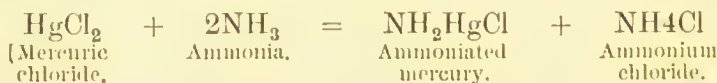


Amino-mercuric
chloride.



Ammoniated
mercury.

Ammoniated mercury is obtained as a white precipitate by pouring an excess of ammonia into a solution of mercuric chloride.



Fusible white precipitate [$\text{HgCl}_2(\text{NH}_3)_2$] is prepared by adding a solution of mercuric chloride to a boiling solution of ammonium chloride and ammonia.

Mercuric sulphide (HgS).—This exists in nature as cinnabar; it constitutes the pigment *vermilion*, which is prepared by rubbing together mercury and sulphur, when the black amorphous mercuric sulphide is obtained, which on heating sublimes as vermilion; the composition of the sulphide is not changed by the heat, but the black

amorphous sulphide becomes converted into the red crystalline variety. *Ethiop's mineral*, formerly employed in medicine, is a mixture of the black mercuric sulphide and free sulphur; it is obtained by rubbing mercury with excess of sulphur.

Mercuric oleate.—This substance, which is now frequently used as an external application in certain skin diseases, is prepared by dissolving yellow mercuric oxide in oleic acid.

Test for Mercury

All solid mercury compounds, if mixed with lime or sodium carbonate, and then heated in a dry test-tube, yield a sublimate of metallic mercury on the cool sides of the tube; this sublimate, when rubbed with a glass rod, produces the characteristic globules of mercury.

Tests for Mercuric Salts

1. Sulphuretted hydrogen gives a black precipitate of mercuric sulphide; if the solution of the mercuric salts is strong, the precipitate may at first come down of a yellowish-white colour; afterwards, as more sulphuretted hydrogen passes in, the light-coloured precipitate passes through successive stages of dark yellow, orange, and brown, to a black colour; these colour stages are due to the gradual displacement of the acid radicle of the mercury salt by the sulphur:

2. Ammonium sulphide also precipitates the black mercuric sulphide.

3. Potassium iodide gives with a solution of a mercuric salt a precipitate of red mercuric iodide, the precipitate being thrown down at first of a yellowish colour, rapidly changing to red; it is soluble in excess either of the mercuric salt or of potassium iodide, but especially the latter.

4. If a solution of a mercuric salt is acidified with a few drops of hydrochloric acid, and then boiled for a few minutes with a strip of bright copper foil, the metal mercury is deposited on the surface of the strip of copper, giving to it a characteristic lustre resembling polished silver; if the strip of copper is washed with water, carefully dried, and then heated in a dry test-tube, a sublimate of metallic mercury will be obtained on the sides of the tube; this sublimate, when rubbed with a glass rod, produces the characteristic globules of mercury; or a scale of iodine may be introduced to the bottom of the tube, which is then gently warmed so as slightly to volatilise the iodine; the vapour of the iodine unites with the mercury, and converts it into the yellow iodide, which in its turn changes to the scarlet mercuric iodide.

5. Caustic potash and caustic soda both give with solutions of mercuric salts a yellow precipitate of mercuric oxide.

Tests for Mercurous Salts

1. Hydrochloric acid gives with a solution of a mercurous salt a white precipitate of mercurous chloride (calomel); this is blackened by the addition of ammonia, owing to the formation of the black mercurous ammonium chloride ($\text{NH}_2\text{Hg}_2\text{Cl}$), the mercurous analogue of ammoniated mercury (NH_2HgCl).

2. Potassium iodide gives a dirty-green precipitate of mercurous iodide.

3. Caustic potash and caustic soda both give a black precipitate of mercurous oxide.

THE FOUR METALS COMPARED

It will be noticed that the metals treated in this

chapter all appear in the right-hand half of the second column in the periodic table on page 88. It will be convenient to note here some points of resemblance and difference. They are all ductile metals and are divalent ; their volatility increases as their atomic weight rises ; thus, zinc boils at 940° , cadmium at 760° , mercury at 357° . Magnesium, zinc, and cadmium all burn with a flame when heated in air, forming the oxides MgO , ZnO , CdO ; they all form sulphates which are isomorphous and have the formula $\text{MgSO}_4 + 7\text{H}_2\text{O}$, etc. ; these sulphates are soluble in water. The spectra of these three elements present many points of similarity. Mercury differs in several respects from the other member of the group : thus it forms two oxides, its sulphate is anhydrous, and it does not burn with flame when heated in the air.

CHAPTER V

ALUMINIUM—TIN—LEAD

Aluminium: Natural Compounds of Aluminium—Preparation and Properties of the Metal—Alums—Aluminium Salts—Tests for Aluminium. Tin: Preparation and Properties of the Metal—Tin Salts—Tests for Tin. Lead: Occurrence in Nature—Preparation and Properties of the Metal—Oxides of Lead—Lead Salts—Tests for Lead. —

ALUMINIUM

Symbol, Al; triad; atomic weight, 27; specific gravity, 2.57; melts at 657°.

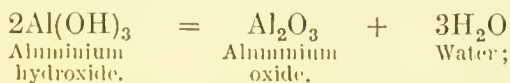
Natural compounds of aluminium.—1.

Aluminium occurs largely in nature combined with silica; the different forms of *clay* consist of aluminium silicate; *felspar*, *granite*, *mica*, *alum-shale* or *schist*, all contain aluminium silicate. 2. *Cryolite* is a double fluoride of aluminium and sodium. 3. *Bauxite* is an impure form of aluminium hydrate. 4. The precious stones, the *ruby* and the *sapphire*, and the polishing powder known as *emery powder*, consist mainly of aluminium oxide or alumina (Al_2O_3).

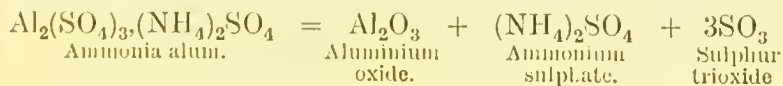
Preparation and properties of the metal aluminium.—The oxide of aluminium cannot be deprived of its oxygen by means of charcoal at any temperature, since the reaction $\text{Al}_2\text{O}_3 + 3\text{C}$ is endothermic and is attended with the *absorption* of a large amount of heat. The metal can be obtained by reducing aluminium chloride by means of the

metal sodium, the sodium uniting with the chlorine, and the metal aluminium being set free. All the aluminium at the present time is obtained by the aid of electricity; pure alumina (Al_2O_3) is dissolved in fused cryolite ($3\text{NaF}, \text{AlF}_3$), and the melted liquid decomposed by a powerful current of electricity; the oxygen of the alumina combines with the carbon anode, while the metal collects at the bottom of the vessel, which forms the kathode. Aluminium is a light, white metal, remaining unchanged in both dry and moist air. Dilute sulphuric and hydrochloric acids both act on the metal aluminium, forming respectively the sulphate and chloride, with evolution of hydrogen. It is practically unaffected by nitric acid; it is dissolved by alkalis and by organic acids in the presence of sodium chloride. It is much used for telescopes, opera-glasses, cooking vessels, etc., on account of its lightness. It forms a valuable alloy with copper, aluminium bronze, which is almost as strong as steel and has the advantage of not rusting. The alloy usually contains 10 per cent. of aluminium. Aluminium is a good conductor of electricity and a very powerful reducing agent.

Aluminium oxide or alumina (Al_2O_3).—This oxide may be prepared either by heating the precipitated aluminium hydroxide.



or by heating ammonia alum, when ammonium sulphate and sulphur trioxide will be volatilised by the heat, the aluminium oxide being left.



Aluminium hydroxide $[\text{Al}(\text{OH})_3]$ is prepared by the addition of ammonium hydrate to an aqueous solution of ammonia alum or potash alum; it is a gelatinous precipitate, which possesses the power of fixing or combining with vegetable dyes, and hence is used as a mordant; it is also employed in the chemical treatment of sewage.

ALUMINIUM SALTS

Ammonia alum $[\text{Al}_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4, 24\text{H}_2\text{O}]$.—This is prepared by mixing solutions of aluminium sulphate and ammonium sulphate, evaporating the mixed solution and setting it aside, when the alum crystallises out. The aluminium sulphate is obtained either by the action of strong sulphuric acid with heat on clay, or by roasting alum-shale in the air. Alum-shale is a hardened clay containing iron pyrites (FeS_2); when roasted the sulphur becomes oxidised to sulphuric acid, which forms aluminium sulphate by its action on the silicate, ferric oxide being also produced; on boiling the roasted shale with water, the aluminium sulphate is dissolved out, ferric oxide being left insoluble.

Potash alum $[\text{Al}_2(\text{SO}_4)_3, \text{K}_2\text{SO}_4, 24\text{H}_2\text{O}]$.—This is prepared by a process similar to that used for making ammonia alum, with the substitution of potassium sulphate for ammonium sulphate.

If potash alum be deprived of its water of crystallisation by heating, the anhydrous alum is known as *burnt alum*.

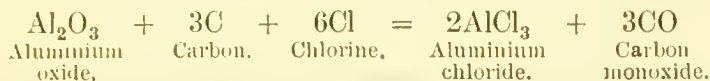
There are *alums* which contain no aluminium, such as *iron alum* $[\text{Fe}_2(\text{SO}_4)_3, \text{K}_2\text{SO}_4, 24\text{H}_2\text{O}]$, and *chrome alum* $[\text{Cr}_2(\text{SO}_4)_3, \text{K}_2\text{SO}_4, 24\text{H}_2\text{O}]$; so that the term “alum” is used for bodies which may or may not contain aluminium. The term alum when used in this extended sense simply means a double sulphate, having the formula $\text{M}_2'''(\text{SO}_4)_3\text{M}_2'\text{SO}_4$

$24\text{H}_2\text{O}$ (where M''' may be aluminium, ferric iron, chromium or manganese, and M' potassium, sodium, ammonium, rubidium, silver, etc.), and crystallising in octahedra, isomorphous (see page 43) with common alum.

Description.—Colourless, transparent, octahedral crystals.

Ordinary impurities.—Iron, and other metals.

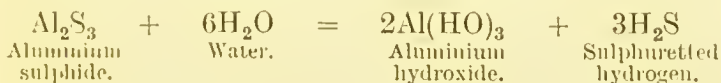
Aluminium chloride (AlCl_3) is prepared by passing a stream of chlorine over a mixture of alumina and charcoal raised to a red heat, when the aluminium chloride volatilises and condenses on cooling to a white solid.



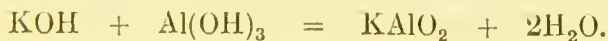
Tests for Aluminium

1. Aluminium salts give with solution of ammonia a white gelatinous precipitate of aluminium hydroxide $\text{Al}(\text{OH})_3$, insoluble in excess of ammonia.

2. With ammonium sulphide aluminium salts also give a precipitate of aluminium *hydroxide*, sulphuretted hydrogen being evolved. Ammonium sulphide does not precipitate the sulphide, because aluminium sulphide is decomposed by water into the hydroxide and sulphuretted hydrogen.



3. With the fixed alkalies, caustic potash and caustic soda, aluminium salts yield a precipitate of aluminium hydroxide, soluble in excess of either fixed alkali, with formation of a soluble alkaline aluminate, thus :—



4. If a solid aluminium compound be heated on charcoal before the blowpipe, it leaves an infusible mass of Al_2O_3 , which glows in the flame; if this be moistened with $\text{Co}(\text{NO}_3)_2$ and again made red hot, a fine blue mass is obtained.

Aluminium is the only commonly occurring metal in the third column of the periodic table (page 88). The other metals in this group are rare. Indium and gallium have already been referred to (page 84).

TIN

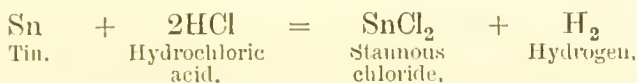
Symbol, Sn; tetrad (dyad in stannous compounds); atomic weight, 119; specific gravity, 7.3; melts at 232°.

Natural compounds of tin.—The principal tin ore is *tinestone* or stannic oxide (SnO_2), which is found in Cornwall, Saxony, Bohemia, Peru, Mexico, Banca, and Australia.

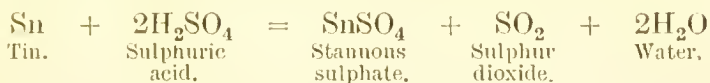
Preparation and properties of the metal tin.—The tin ore is first roasted to expel arsenic and sulphur, and the stannic oxide is then reduced to the metallic state by heating it with anthracite coal or powdered charcoal. Tin is a soft and very malleable metal; it can therefore be rolled out into thin foil (tin-foil). It does not lose its lustre on exposure to the air at ordinary temperatures, and is used to coat iron to prevent the latter from rusting, *tin-plate* consisting of thin sheets of iron coated with tin. A bar of tin when bent emits a peculiar noise, the so-called *cry of tin*, produced by the friction of the crystals of the metal against one another. Tin enters into the composition of several very useful alloys: *bronze* or *gun metal* is an alloy of copper and tin; *britannia metal* is composed of tin and antimony; *solder* consists of tin and lead; *pewter* is also an alloy of tin and lead. With mercury it

forms an amalgam used to coat the backs of looking-glasses.

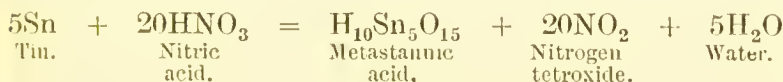
Action of acids on the metal tin (see page 75). — Hot concentrated hydrochloric acid forms stannous chloride (SnCl_2) with evolution of hydrogen.



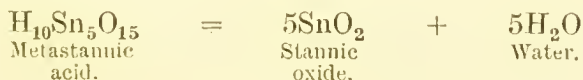
Hot strong sulphuric acid forms stannous sulphate (SnSO_4), and liberates sulphur dioxide.



Strong nitric acid acts energetically on tin with the production of a white powder, metastannic acid, and the evolution of nitrogen tetroxide.



Stannic oxide (SnO_2) is prepared by heating metastannic acid, the product of the action of nitric acid on tin.



Stannic oxide is used, under the name of *putty-powder*, as a polishing powder for plate, lenses, etc.

TIN SALTS

There are two classes of tin salts, *stannous* and *stannic*. In the former the tin is only exerting one half of its full valency and is a dyad; in the latter it is exerting its full valency and is a tetrad:

Stannous chloride ($\text{SnCl}_2, 2\text{H}_2\text{O}$) is prepared by the action of hot concentrated hydrochloric acid on tin. This salt is used commercially, under the name of *tin-salt*, in dyeing and for purposes of reduction. It occurs in colourless, rather deliquescent, crystals.

Stannic chloride (SnCl_4) is prepared by passing chlorine into a solution of stannous chloride, or by passing dry chlorine over melted tin; it is a colourless fuming liquid.

Tests for Tin

1. Sulphuretted hydrogen gives with an acidified solution of a stannous salt a brownish-black precipitate of stannous sulphide (SnS), and with an acidified solution of a stannic salt a yellow precipitate of stannic sulphide (SnS_2); both sulphides are soluble in yellow ammonium sulphide, with formation of ammonium thio-stannate $(\text{NH}_4)_2\text{SnS}_3$.

When this solution is acidulated with hydrochloric acid the tin is reprecipitated only as *yellow* SnS_2 .

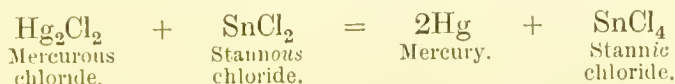


The change of colour from brown to yellow is therefore useful confirmatory evidence in the case of *stannous* compounds.

2. Soluble stannous salts act as reducing agents, whereas stannic salts have no reducing action. For instance, if a solution of stannous chloride be added to a solution of mercuric chloride, calomel (mercurous chloride) will be thrown down. The *stannous* salt is oxidised and the mercuric salt is reduced.



If more stannous chloride be now added, the reduction is carried still further, the calomel being wholly or partly reduced to the metal mercury in a fine state of division, and more stannic chloride being produced.



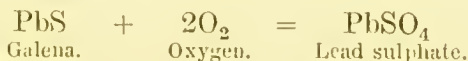
3. If a solid tin compound be heated on charcoal with potassium cyanide and sodium carbonate, a white malleable globule of tin is obtained.

LEAD

Symbol, Pb; tetrad (but only uses dyad valency in its common salts); atomic weight, 207; specific gravity, 11.2; melts at 326°.

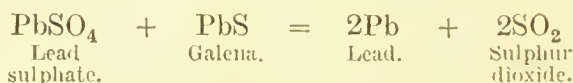
Natural compounds of lead.—The principal lead compound occurring in nature is *galena*, sulphide of lead (PbS), which always contains small quantities of sulphide of silver; lead is also naturally found in small quantities as the sulphate and carbonate.

Preparation of the metal lead.—The principal process for the extraction of lead from galena is known as the *air reduction process*. It consists in roasting the galena in a furnace in a current of air, so as to convert it, in part, into the sulphate and oxide.



The current of air is then shut off, and the temperature of the furnace is raised, when the undecomposed galena reduces both the sulphate and oxide

to the metallic state, with evolution of sulphur dioxide.



Lead thus prepared contains silver; this, if present in sufficient quantity to pay for its extraction, is obtained by converting the lead into

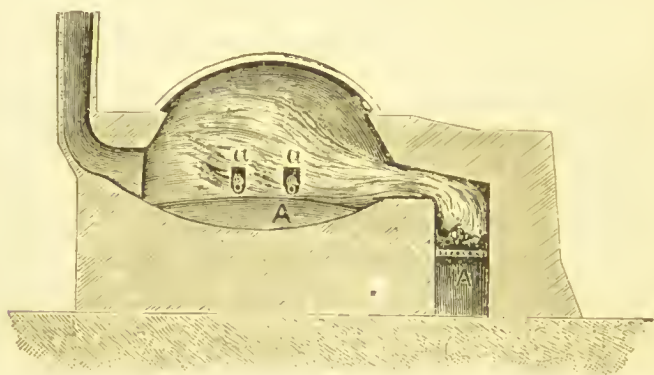


Fig. 33.—Section of the furnace employed in the cupellation process.

lead oxide, which is removed, the silver remaining unchanged. The process by which this is effected is called the *cupellation process*; it consists in roasting the lead in a reverberatory furnace (Fig. 33), the floor or hearth of which is lined with porous clay or bone-ash; the lead *A* melts and oxidises to lead oxide under the influence of blasts of air admitted through openings *aa*; most of this lead oxide in a molten condition flows away by side openings, while the remainder is absorbed by the porous clay or bone-ash, pure silver being finally left on the hearth of the furnace in a molten state.

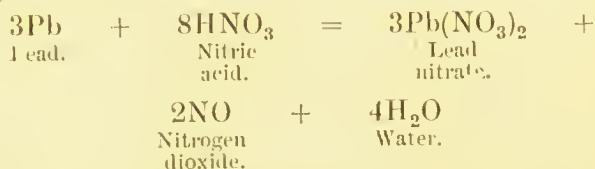
From the lead oxide produced in this process, metallic lead may be obtained by reduction with charcoal or coal. The removal of silver from a quantity of lead, in the metallic state, may be effected by means of *Pattinson's process*, which depends upon the fact that the metal lead is less easily fusible than an alloy of silver and lead. The lead containing the silver is melted and then allowed to cool gradually; the part solidifying out first consists of crystals of pure lead, which can be raked out by means of a perforated iron ladle; by a systematic repetition of this process, lead containing 3 to 4 oz. of silver per ton can be separated into a portion containing less than 1 oz. per ton and a rich alloy containing 75 to 80 oz., which is submitted to the cupellation process. Small quantities of silver can also be separated from molten lead by agitating it with 5 per cent. of zinc; the zinc dissolves out the silver, and the zinc-silver alloy rises to the top. The zinc is then separated from the silver by distillation. (*Parkes' process.*)

Properties of the metal lead.—Lead is a lustrous, bluish-grey metal, soft enough to be cut with a knife, and to leave a mark on paper when drawn across it; it is malleable and ductile, but is not a good conductor of heat and electricity as compared with many other metals. If lead is exposed to perfectly dry air, it does not oxidise or tarnish, but if exposed to moist air, it soon becomes covered with a film of basic carbonate of lead; similarly, if lead is immersed in distilled water *which has been boiled* to deprive it of all dissolved air, it remains unaffected by the water, but soft water containing air in solution attacks lead, the oxygen of the air forming lead oxide, which is then dissolved by the water as lead hydroxide in small but appreciable quantities. This is one way in which a drinking water, passing through leaden pipes, may become

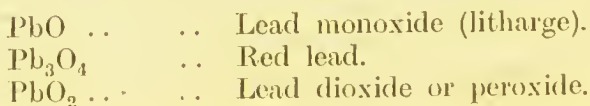
contaminated with lead. The corrosive action of a water on lead is much increased by the presence in it of chlorides, nitrates, nitrites, and of ammonia, whereas the presence of sulphates, of calcium carbonate (held in solution as bicarbonate by a *moderate* excess of carbon dioxide), and of phosphates, hinders corrosion. Some soft waters, notably some moorland waters, have a powerfully solvent action upon lead, due in some cases, perhaps, to the presence of acids in the water, either humic or ulmic acid derived from the soil, and whole villages have thus been poisoned. Hard water, such as that from the Thames, the Trent, etc., does not act appreciably upon lead.

Metallic lead is largely used in the manufacture of pipes, as a covering for roofs, etc. Lead is a constituent of several alloys; the most important are: *type-metal*, an alloy of lead, antimony, and tin; *pewter* and *soft solder*, alloys of lead and tin; *shot*, an alloy of lead with a small quantity of arsenic (not more than 0·8 part in 100), which possesses the property of hardening the lead.

Action of acids on the metal lead (see page 74).—Hydrochloric and sulphuric acids have no action on lead in the cold, and attack it only slowly when boiling and concentrated. Nitric acid readily acts on lead, forming lead nitrate, and evolving nitrogen dioxide.

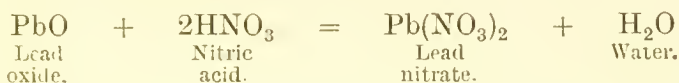


Lead oxides. — There are three important oxides of lead, the *monoxide*, the *dioxide*, and *red lead*.



Lead oxide (PbO) is prepared by the oxidation of the metal lead, by roasting it in air. In the amorphous state it forms a dirty yellow powder (*massicot*); if fused and solidified, it forms brighter, reddish-yellow scales (*litharge*).

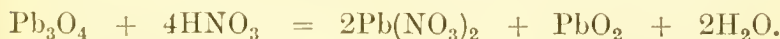
This oxide is largely used in the manufacture of flint glass, and as a cheap glaze for earthenware. Warm dilute nitric acid dissolves litharge *completely*, forming lead nitrate and water.



Acetic acid also dissolves litharge, forming lead acetate.

Ordinary impurities.—Copper, iron, carbonate.

Red lead (Pb_3O_4), also known as *minium*, is prepared by heating lead oxide (PbO) in air to 400° for some time, when it absorbs oxygen and, becoming of a bright red colour, produces red lead. If red lead be strongly heated, it liberates the oxygen absorbed from the air, and returns to the condition of litharge. Warm dilute nitric acid dissolves only two-thirds of the lead, leaving the other third as brown lead dioxide (PbO_2).



The action of warm dilute nitric acid, therefore, enables us to distinguish litharge from red lead.

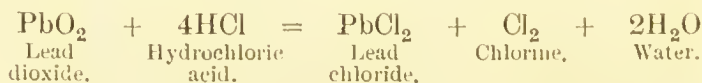
Hydrochloric acid warmed with red lead forms lead chloride with evolution of chlorine.



Lead dioxide (PbO_2) is also known as *lead peroxide*, and, on account of its brown colour with a purple tinge, is sometimes called the *puce-coloured oxide* of

lead. It is obtained, as previously stated, by the action of nitric acid on red lead. On account of this action of nitric acid, it has been suggested that red lead is a compound of two molecules of litharge combined with one molecule of the peroxide ($2\text{PbO}, \text{PbO}_2$).

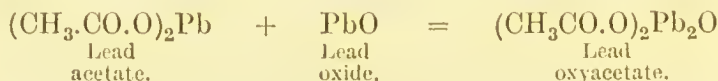
Lead dioxide if heated loses one-half of its oxygen, and is converted into the monoxide; hydrochloric acid acts on it, forming lead chloride, with evolution of chlorine. In this respect it behaves like most peroxides, which can thus be distinguished from oxides.



SALTS OF LEAD

Lead acetate $[(\text{CH}_3\text{CO.O})_2\text{Pb}.3\text{H}_2\text{O}]$. — This salt, on account of its sweet taste, is commonly known as *sugar of lead*; it is prepared by dissolving litharge in acetic acid with heat, as described on page 577.

Lead oxyacetate $[(\text{CH}_3\text{CO.O})_2\text{Pb}_2\text{O}]$. — This basic lead acetate is prepared by boiling a solution of lead acetate with lead oxide.



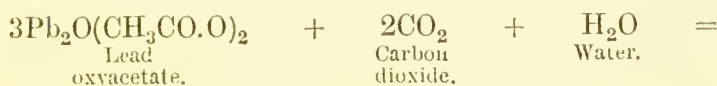
Liquor plumbi subacetatis fortis is a strong solution of this oxyacetate, and is frequently termed *Goulard's extract*; a weaker solution of it is the *liquor plumbi subacetatis dilutus*, which is frequently used as a lotion, and is commonly known as *Goulard water*.

Lead nitrate $[\text{Pb}(\text{NO}_3)_2]$. — We have already seen that this salt is formed by the action of nitric

acid on litharge, or on red lead, or on the metal lead. Its actual preparation is described in detail on page 576.

White lead, or basic lead carbonate [$2\text{PbCO}_3, \text{Pb}(\text{OH})_2$].—This substance, which is so largely used as a white paint, is not the normal lead carbonate (PbCO_3), but a basic carbonate of lead. There are two methods of preparing it.

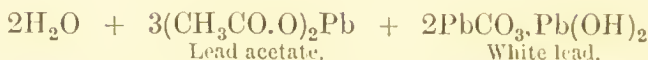
1. *The English or French process* consists in passing carbon dioxide gas through a solution of lead oxyacetate, when that portion of the lead not in union with the acetic radicle is precipitated as *white lead*.



The lead acetate remaining in solution can then be boiled with litharge, and so a fresh batch of the oxyacetate will be obtained for further treatment with carbon dioxide.

2. *The Dutch process* also consists in decomposing lead oxyacetate with carbon dioxide in presence of moisture, but an entirely different arrangement is adopted.

Metallic lead is cast into gratings, so as to expose as large a surface of the metal as possible, and these are suspended in earthenware pots containing a layer of vinegar at the bottom; the pots are embedded in spent tan spread on the floor of a shed. The acetic acid of the vinegar and the oxygen of the air attack the lead, forming an oxyacetate, which is immediately decomposed, by the carbon dioxide and moisture evolved from the fermenting spent tan, into white lead.



The action is allowed to go on until the conversion is complete, when the "stack" is taken down, and the white lead ground and washed. White lead prepared by this process is more compact, or has more *body*, than that made by the English or French process, and is therefore preferred for painting purposes. When used as a paint, white lead slowly darkens, from traces of sulphuretted hydrogen in the air, forming the black sulphide of lead.

Description.—A soft, heavy, white powder, soluble with effervescence in dilute nitric acid or in acetic acid.

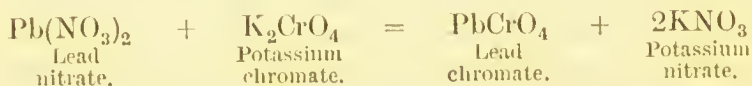
Ordinary impurities.—Zinc, calcium, barium, magnesium; sulphate.

Lead iodide (PbI_2) is prepared by precipitating a solution of lead acetate or lead nitrate with potassium iodide, as described in detail on page 576.

Description.—Obtained as above, iodide of lead is a bright yellow-coloured precipitate insoluble in cold water, but soluble in hot water; as the hot aqueous solution cools, the iodide crystallises out in hexagonal plates.

Ordinary impurities.—Acetate, nitrate; potassium.

Lead chromate (PbCrO_4) is prepared by precipitating a solution of lead acetate or lead nitrate with potassium chromate.



Lead chromate is a bright yellow precipitate, and

is used as a pigment under the name of *chrome-yellow*. If boiled with caustic potash or caustic soda it yields *chrome-red* (PbCrO_4 , PbO), an orange-red pigment.

Tests for Lead

1. Sulphuretted hydrogen gives a black precipitate of lead sulphide. This is the test employed for the detection of lead in a drinking water, the absence of other metals yielding precipitates with sulphuretted hydrogen being proved; if lead is present in the water, a brownish or blackish colour, according to the amount present, will be produced on the addition of sulphuretted hydrogen.

2. Ammonium sulphide also precipitates the black lead sulphide.

3. Potassium chromate gives a yellow precipitate of lead chromate, changing to an orange-red colour on boiling with caustic potash or caustic soda.

4. Dilute sulphuric acid gives with solutions of lead salts a white precipitate of lead sulphate.

5. Potassium iodide gives a bright yellow precipitate of lead iodide, soluble in boiling water, and crystallising out in golden-coloured spangles as the solution cools.

6. Hydrochloric acid gives with moderately strong solutions of lead salts a white precipitate of lead chloride; this precipitate remains unaltered on the addition of solution of ammonia, thus distinguishing it from mercurous chloride, which is also thrown down as a white precipitate by hydrochloric acid from a solution of a mercurous salt. Hydrochloric acid does not completely precipitate lead from its solutions, as lead chloride is appreciably soluble in cold water, and more so in hot water.

7. If a solid lead compound be heated on char-

coal with Na_2CO_3 , a malleable globule of lead is obtained, surrounded by a yellow incrustation.

TIN AND LEAD COMPARED

The metals tin and lead have several points of resemblance; they are both soft, malleable, easily reducible metals. When heated in the air they form oxides. They are bivalent and tetravalent, and form two oxides (SnO , SnO_2) and two chlorides (SnCl_2 , SnCl_4), etc. They belong to the same family of elements as the non-metals, carbon and silicon. The highest oxides of tin and lead show feeble acid properties, but their salts, the stannates and plumbates, are very unstable.

CHAPTER VI

ARSENIC—ANTIMONY—BISMUTH

Arsenic: Occurrence in Nature—Arsenious and Arsenic Compounds—Tests for Arsenic. Antimony: Occurrence in Nature—Antimony Salts—Tests for Antimony. Bismuth: Bismuth Salts—Tests for Bismuth—Points of Family Likeness in the Members of the Nitrogen Family.

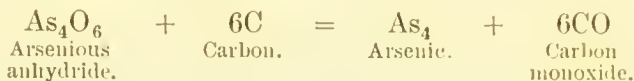
ARSENIC

Symbol, As; molecule, As₄; pentad and triad; atomic weight, 75; molecular weight, 300; specific gravity, 5.7.

THE molecules of arsenic and phosphorus are tetra-atomic (*see* page 44); their molecular weights are, accordingly, four times their atomic weights.

Natural compounds of arsenic.—1. The commonest arsenical ore is mispickel or arsenical iron pyrites (FeSAs). 2. Two compounds of arsenic and sulphur occur in nature, a yellow sulphide named *orpiment* (As₂S₃), and a red sulphide named *realgar* (As₂S₂). 3. *Arsenious acid* (H₃AsO₃) occurs in minute amounts in several mineral springs, as in those of Ems, Kissingen, Pyrmont, and Schwalbach. The quantity of arsenious acid present in these waters is too small to confer poisonous properties on them when drunk, but it is quite possible that their therapeutic properties are in part due to the minute quantities of arsenic present. 4. The element *arsenic* occurs native to a small extent.

Preparation of arsenic.—The element arsenic is obtained as a sublimate by passing the vapour of arsenious anhydride or white arsenic (As_4O_6) over heated charcoal.



Properties of the element.—Arsenic possesses a steel-grey colour and a metallic lustre; a yellow allotropic variety has recently been obtained.* The element is very brittle, and is therefore easily pulverised. When heated in the air, arsenic volatilises and burns, forming arsenious oxide or white arsenic (As_4O_6), and emitting at the same time an unpleasant garlic-like odour. Arsenic begins to volatilise at 100° , it passes rapidly into vapour at 180° , and can be melted (500°) only under pressure. The only use to which arsenic is put is in the manufacture of shot, which consist of lead alloyed with a small amount of arsenic.

COMPOUNDS OF ARSENIC

Two classes of arsenical compounds exist, viz. the *arsenious compounds*, in which the arsenic is only exerting the valency of a triad; and the *arsenic compounds*, in which the arsenic is exerting its full valency as a pentad.

There are two oxides of arsenic, arsenious anhydride and arsenic anhydride, or arsenic pentoxide.

Arsenious anhydride (As_4O_6).—This oxide constitutes the *white arsenic* of commerce. It is obtained during the smelting or roasting of arsenical iron pyrites and other ores containing arsenic united with sulphur, the latter element burning away as sulphur dioxide, whilst the arsenic volatilises and

* Chemical Society's Annual Reports, 1904, p. 33.

oxidises to arsenious oxide, which is then condensed to a solid in long condensing flues attached to the smelting furnace.



There are two varieties of arsenious anhydride—(1) a crystalline variety which can be obtained in small octahedra, and (2) a vitreous variety constituting the deposit in the condensing flues attached to the furnaces in which arsenical ores are being roasted; this vitreous variety is obtained at first as a semi-transparent, glass-like solid, becoming after a time opaque, like porcelain. The white arsenic of commerce is obtained by grinding this vitreous variety to a powder. Arsenious anhydride, or white arsenic, is a white, odourless, and almost tasteless substance, possessing a very faint sweetish taste; it is very poisonous, 2 to 4 grains being usually a poisonous dose; in cases of poisoning with arsenic the administration of freshly-precipitated ferric hydrate or of solution of dialysed iron will act as an antidote, although not a very efficacious one, by forming the insoluble arseniate of iron. Arsenious anhydride is soluble in cold water to the extent of half a grain in a fluid drachm, and in boiling water to the extent of 6 grains in a fluid drachm; when dissolved in water it forms arsenious acid (H_3AsO_3). The specific gravity of the vapour of arsenious oxide is 198, its molecular weight is therefore $198 \times 2 = 396$, which gives the formula As_4O_6 . Probably it will be found that at some high temperature (see page 46) dissociation occurs, and a molecule, As_2O_3 , is obtained. It seems, indeed, that we may expect this temperature to be in the neighbourhood of 1800° .

Arsenic anhydride, or arsenic pentoxide (As_2O_5).—This, the higher oxide of arsenic, is obtained by the oxidation of arsenious oxide with nitric acid; if ordinary white arsenic be heated with nitric acid, reddish-brown fumes of oxides of nitrogen are evolved, and the residue, if dried and raised to a low red heat to expel water, leaves the arsenic anhydride.

Arsenic anhydride is a white amorphous substance, dissolving in water to form arsenic acid (H_3AsO_4); although more soluble in water than arsenious oxide, it is less poisonous than that substance. At temperatures above a red heat arsenic anhydride breaks up into arsenious anhydride and oxygen.

There are two acids of arsenic corresponding to the two anhydrides, viz. arsenious acid and arsenic acid.

Arsenious acid (H_3AsO_3).—This is prepared by dissolving white arsenic (arsenious anhydride) in water.

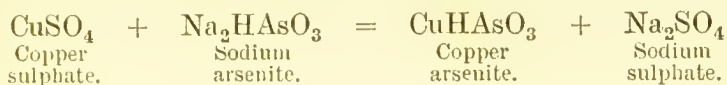


It is a *weak* acid (*see* page 106), and is only slightly soluble in water; it is too weak to decompose solutions of the alkaline carbonates. Arsenious acid is contained in two solutions used in medicine, both of them containing 1 per cent. of arsenic in solution; these are Fowler's solution (*liquor arsenicalis*) and the hydrochloric solution of arsenic (*liquor arsenici hydrochloricus*). Although arsenious acid is so sparingly soluble in cold water, yet it is much more soluble in a dilute solution of an alkaline carbonate, or in a weak mineral acid. On this account Fowler's solution contains some potassium carbonate, which merely increases the solubility of the arsenious acid; and the hydrochloric solution of arsenic contains

some diluted hydrochloric acid, which also increases the solubility of arsenious acid.

Two compounds of arsenious acid are not uncommonly employed as pigments, viz. Scheele's green (arsenite of copper) and emerald green (aceto-arsenite of copper).

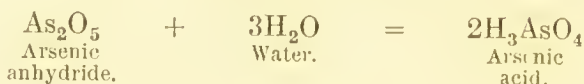
Scheele's green is prepared by mixing together solutions of copper sulphate and sodium arsenite, when it is thrown down as a bright-green precipitate.



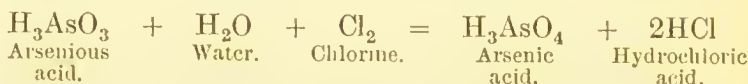
Wall-papers printed with bright green colours are frequently surfaced with Scheele's green or emerald green, the arsenic contained in which may exercise a very injurious influence on people living or sleeping in rooms so papered. The arsenical pigment may become brushed off the paper as dust, and so become disseminated through the atmosphere of the room. But it is not only by this mechanical means that the arsenic can be dispersed into the atmosphere of the room; the papers are fastened to the walls with starch-paste, which easily ferments and sets free nascent hydrogen; and since the paper is originally saturated with the paste, this nascent hydrogen comes directly into contact with the arsenical compounds, and produces gaseous arseniuretted hydrogen, which escapes into and poisons the air of the room. It is true that the quantity of the gas so produced is very minute; but as arseniuretted hydrogen is more poisonous than any other compound of arsenic, very small quantities may be sufficient to produce very injurious effects.

For the methods of detecting arsenic in wall-papers, see pages 341, 343.

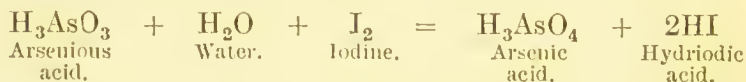
Arsenic acid (H_3AsO_4).—This is obtained by dissolving arsenic anhydride in water.



It may also be prepared by the action of chlorine on a solution of arsenious acid, the chlorine uniting with the hydrogen of some of the water to form hydrochloric acid, and setting free oxygen, which in the nascent state oxidises the arsenious acid to arsenic acid.



A similar action occurs when iodine is added to a solution of arsenious acid.

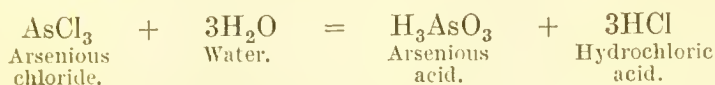


Arsenic acid is a stronger acid as regards its action on litmus paper, and its power of forming salts, than arsenious acid, and is much more soluble in water, but it is not so powerful a poison as arsenious acid. Arsenic acid is employed in the preparation of magenta and some other aniline dyes, becoming reduced to arsenious acid during the process. If the dye is not properly freed from the arsenious acid, then injurious effects may follow from the employment of articles coloured with such dyes, such as socks, gloves, cretonne, and other hangings. Red aniline dyes are also sometimes used for giving a colour to liqueurs, syrups, sweetmeats, and raspberry vinegar; and here, again, injurious effects might follow from the taking of such coloured articles if the dye contained arsenic. A potassium arseniate

(K_2HAsO_4) is contained in some fly-papers, flies being readily killed by imbibing a small quantity of a solution of this salt.

Two salts of arsenic acid are used in medicine, viz. sodium arseniate (see page 279) and ferrous arseniate (see page 372).

Arsenious chloride ($AsCl_3$) is prepared by burning powdered arsenic in dry chlorine, or by distilling a mixture of arsenious anhydride, sodium chloride, and concentrated sulphuric acid. It is a colourless, oily liquid, decomposed by water into arsenious and hydrochloric acids.



Arsenious iodide (AsI_3) is prepared by direct union of its elements, or by dissolving arsenious anhydride in hydriodic acid. An aqueous solution, containing 1 per cent. of this arsenious iodide and 1 per cent. of mercuric iodide, with an excess of potassium iodide, forms Donovan's solution (*liquor arsenii et hydrargyri iodidi*, B. P.).

Tests for Arsenic

1. Sulphuretted hydrogen gives, with an acid solution of arsenious acid, a yellow precipitate of arsenious sulphide, which is soluble in alkalies and in ammonium sulphide.

2. If a small quantity of white arsenic is mixed with a reducing agent containing carbon, such as *black flux* (a mixture of potassium carbonate and charcoal, obtained by heating acid tartrate of potassium in a covered vessel), and the mixture introduced into a Berzelius's reduction tube, and then heat applied to the bulb containing the mixture, a sublimate of metallic arsenic of an iron-grey colour

will be obtained on the cool part of the tube just above the constriction. (Fig. 34, A being the sublimate of the metallic arsenic.)



Fig. 34.—Sublimate of metallic arsenic in a Berzelius's reduction tube.

If the portion of the tube containing the sublimate A be cut off with a file, and then broken into fragments, and the fragments introduced into a dry test-tube, on applying heat to the bottom of the latter, whilst holding it in an almost horizontal position, with the mouth of the tube partially covered by the thumb, the arsenic will volatilise and oxidise to arsenious oxide, which will deposit on the cool part of the tube in small brilliant crystals, consisting of perfect and imperfect octahedra. If the portion of the tube containing the sublimate be viewed under a microscope, using a $\frac{1}{4}$ -inch or $\frac{1}{5}$ -inch objective, the crystals will present the characteristic appearances shown in Fig. 35.

3. *Reinseh's test*.—This very delicate test for arsenic consists in boiling, for a short time, a strip of bright copper foil in a solution of arsenious acid, to which one-sixth of its volume of hydrochloric acid has been added. Arsenic is deposited on the surface of the copper as a dull grey film. The acid liquid is then poured off from the slip of copper, and the latter washed two or three times with water and dried, firstly by pressure between folds of blotting-paper, and lastly by carefully warming it some distance above the Bunsen flame. The strip of copper, with the deposit of arsenic on it, is now transferred to a dry test-tube and heat is applied in a manner similar to that described in the previous test, when the

arsenic volatilises and oxidises to arsenious oxide, which forms a crystalline deposit on the cool part of the tube, presenting under the microscope the characteristic appearances shown in Fig. 35.

Reinsch's test may be employed for the detection of arsenic in wall-paper. Some of the paper is cut into small pieces, which are then digested in diluted hydrochloric acid with heat for a few minutes; the

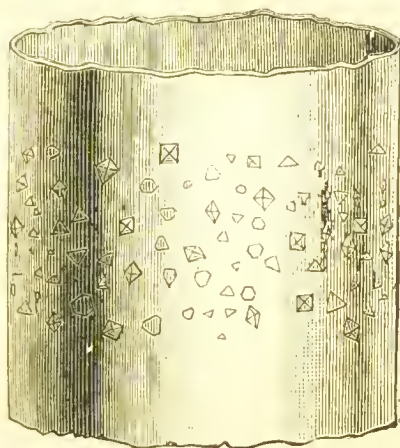


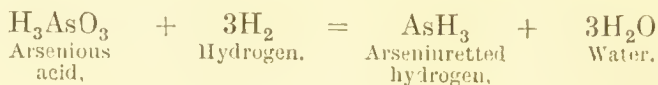
Fig. 35.—Crystals of arsenious oxide (magnified).

acid liquid is poured off, boiled with a strip of bright copper, and the test proceeded with in the manner just described.

4. *Marsh's test*.—This delicate test for arsenic depends upon the conversion of the arsenic into arseniuretted hydrogen, and obtaining from the latter a deposit of metallic arsenic. Hydrogen is generated in a suitable apparatus (Fig. 36) from pure zinc and dilute sulphuric acid; the gas is dried by passing through a calcium chloride tube (A in Fig. 36), and is then ignited as it escapes from the end of the tube bent at right angles.

If some solution of arsenious acid is now poured

into the apparatus by means of the long funnel, the nascent hydrogen produces arseniuretted hydrogen (AsH_3), the production of which is quickly indicated by the hydrogen flame becoming a pale livid colour.



In arseniuretted hydrogen the two elements are so loosely combined that a low red-heat is sufficient

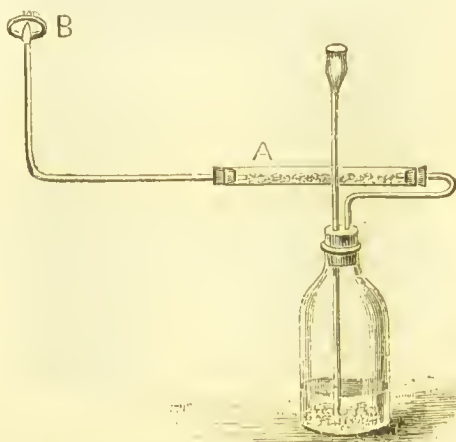


Fig. 36.—Apparatus for Marsh's test.

to decompose the compound into arsenic and hydrogen; the gas, therefore, when passed through a glass tube, the central portion of which is made red-hot, deposits a mirror of metallic arsenic on the cooler parts of the tube just beyond the heated portion. The same decomposition is taking place when arseniuretted hydrogen is inflamed in the air; the high temperature of the flame decomposes the unburnt gas in the interior of the flame into arsenic and hydrogen, and it is this finely-divided metallic arsenic which imparts to the flame its pale livid colour. The presence of the metallic arsenic in the

interior of the flame is readily proved, and constitutes the final stage of Marsh's test; for if a piece of cold white porcelain, such as an evaporating dish or porcelain crucible lid (B in Fig. 36), is pressed down upon the flame for a moment or two, the cold porcelain becomes coated with a round blackish-grey stain of metallic arsenic at the spot where the flame touched it. This spot of metallic arsenic readily dissolves in solution of chlorinated lime or chlorinated soda and so can be distinguished from the antimony spot which is obtained under similar conditions (*see* page 349). To detect arsenic in wall-paper by means of Marsh's test, it is simply necessary to introduce into Marsh's apparatus some of the acid liquid obtained by digesting pieces of the paper in diluted hydrochloric acid with heat, the test being then proceeded with in the usual way.

In employing Marsh's test, care must be taken that no unburnt arseniuretted hydrogen escapes into the atmosphere of the laboratory, as it is a most powerful poison, being, in fact, more poisonous than any other arsenical compound.

If the tube A (Fig. 36) contain a pad of cotton wool impregnated with lead acetate, to intercept any sulphuretted hydrogen that may by chance be evolved, and the issuing gas be allowed to come into contact with a filter paper moistened with silver nitrate solution, a black stain will appear if arsenic is present. If the filter paper be moistened with mercuric chloride solution instead, the stain will be yellow (Gutzeit test).

5. If to an aqueous solution of arsenious acid some copper sulphate be added, and then a drop or two of solution of ammonia, a bright green precipitate (Schcele's green) will be thrown down.

6. If to an aqueous solution of arsenious acid some silver nitrate be added, and then a drop or two

of dilute solution of ammonia, a bright yellow precipitate of silver arsenite will be obtained. This reaction may be applied to the detection of arsenic in wall-paper; about a square inch of the paper, with the coloured surface uppermost, is placed in a small porcelain dish, distilled water is poured on so as just to cover the paper, and a few drops of solution of ammonia are added; after standing for a minute or two, a crystal of silver nitrate is dropped into the dish on to the surface of the piece of paper, when, if arsenic be present, a yellow deposit of silver arsenite will occur around the edge and over the surface of the crystal. This test depends upon the solubility of Scheele's green (copper arsenite) in a weak solution of ammonia, and the precipitation from this solution of the yellow silver arsenite, in presence of an excess of silver nitrate.

Distinction between Arsenious and Arsenic Acids

If to an aqueous solution of arsenic acid some silver nitrate be added, and then a drop or two of solution of ammonia, a *chocolate-coloured* precipitate of silver arseniate will be obtained; this test serves to distinguish between the two acids, as in similar circumstances arsenious acid will give a *bright yellow* precipitate. In like manner, *neutral* solutions of arseniates will at once give a chocolate precipitate, and *neutral* solutions of arsenites a yellow precipitate, with silver nitrate.

Both precipitates are soluble in ammonia solution and also in dilute nitric acid.

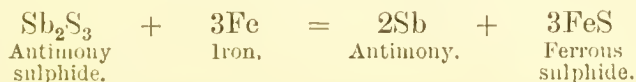
Arsenates do *not* give a yellow precipitate of As_2S_3 , when treated with sulphuretted hydrogen, until the arseniate has been reduced to an arsenite by the long-continued passage of H_2S or by other means.

ANTIMONY

Symbol, Sb ; *pentad* ; *atomic weight*, 120·4 ; *specific gravity*, 6·6 ; *melts*, 630°.

Natural compounds of antimony.—The sulphide of antimony (Sb_2S_3) is the principal natural compound of this metal ; it is known as *grey antimony ore*, and in the form of powder as *black antimony*.

Preparation and properties of the metal antimony.—This is obtained by heating together the native sulphide of antimony and metallic iron, the iron uniting with the sulphur to form ferrous sulphide, and setting free the antimony.



Crude antimony contains arsenic, from which it can be purified by fusing with some sodium carbonate and potassium nitrate, and well stirring the mixture, when the arsenic becomes converted into sodium arseniate.

Antimony is a hard, brittle, white metal ; when heated before the blowpipe it burns, giving a white vapour of the oxide ; it is contained in *type metal*, an alloy of lead and antimony and tin, and in *britannia metal*, an alloy of tin and antimony.

A yellow allotropic variety of antimony has recently been described.*

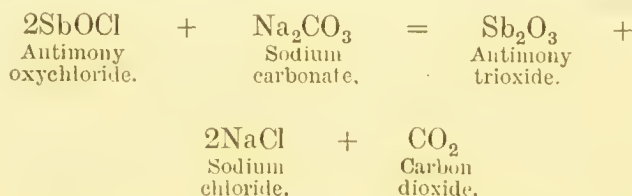
Antimony trioxide or antimonious oxide (Sb_2O_3) is prepared by pouring the acid solution of antimony trichloride into water, by which means a white preeipitate of oxychloride of antimony is thrown down. The composition of this preeipitate

* Chemical Society's Annual Reports, 1904, p. 33

may vary somewhat with the conditions, but the essential reaction is—



This precipitate is then stirred up with solution of sodium carbonate, which abstracts the chlorine from the oxychloride, producing the pure antimony trioxide, which is of a light buff colour.

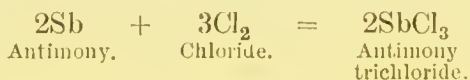


Antimony pentoxide, or antimonic oxide (Sb_2O_5), is prepared by the action of nitric acid on the metal antimony.

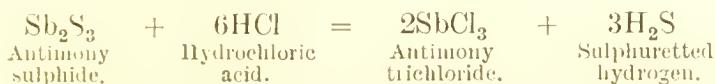
ANTIMONY SALTS

There are two classes of antimony compounds, the *antimonious* and *antimonic*, resembling the two classes of arsenical compounds. In the antimonious compounds the antimony is only exerting part of its valency as a triad, whereas in the antimonic compounds it is exerting its full valency as a pentad.

Antimony trichloride or antimonious chloride (SbCl_3).—1. This may be prepared by direct union of the elements; if powdered metallic antimony is thrown into a jar of chlorine, it will catch fire, producing antimony trichloride.

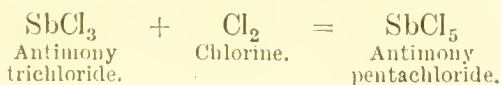


2. The usual method of preparing this chloride is by the action of strong hydrochloric acid with heat on the native sulphide of antimony.

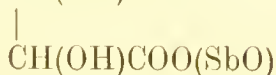
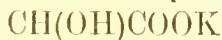


Prepared in this way it is generally of a reddish-brown colour from the presence of iron salts; it is a strongly acid liquid, commonly known as *butter of antimony*, but it is actually a solution of antimony trichloride in hydrochloric acid, since the chloride itself is of a buttery consistence, whence its common name. The true butter of antimony is obtained by evaporating the acid solution to a low bulk, and distilling the residue, when the antimony trichloride condenses in the neck of the retort as a white, semi-transparent mass.

Antimony pentachloride, or antimonic chloride (SbCl_5), is prepared by acting on the trichloride with chlorine.



Tartarated antimony



—This compound, commonly known as *tartar emetic*, is a tartrate of potassium and antimony. It is prepared by mixing antimony trioxide and potassium acid tartrate with sufficient water to form a paste, leaving it for twenty-four hours, as the two substances are somewhat sluggish in uniting, and then boiling the paste with water; on filtering, and concentrating the solution by evaporation, the tartar

emetic is obtained in colourless, triangular crystals, which contain half a molecule of water of crystallisation. Its preparation, in the laboratory, is described on page 578.

It will be noticed in this compound that one of the hydrogen atoms of the tartaric acid is replaced by the metal potassium, and the other, not by the *metal* antimony, but by the univalent radicle ($-\text{Sb}=\text{O}$).

Ordinary impurities.—Chloride, sulphate; other metals.

Sulphurated antimony.—Prepared by boiling native black sulphide of antimony and sulphur with solution of caustic soda, filtering and precipitating the sulphurated antimony with diluted sulphuric acid, when it is thrown down as an orange-red precipitate. It is a mixture of the sulphides and oxides of antimony, and is one of the many varieties of *mineral kermes*, so called from their similarity in colour to the *insect kermes*: *kermes* being the old name of the cochineal insect.

Description.—A dull-red powder, soluble in caustic soda. Evolves sulphuretted hydrogen when warmed with hydrochloric acid.

Ordinary impurity.—Arsenic.

Tests for Antimony

1. Hydrochloric acid gives, with a neutral solution of an antimony salt (such as tartar emetic), a white precipitate of oxychloride of antimony, soluble in excess of hydrochloric acid; if this solution be poured into water the oxychloride is again precipitated.

2. Sulphuretted hydrogen gives, with an aqueous solution of an antimony salt, acidulated with dilute hydrochloric acid, an orange-red precipitate of

antimony sulphide (Sb_2S_3), soluble in alkalies and in ammonium sulphide, and in strong hydrochloric acid.

3. If a solution of an antimony salt, to which sufficient hydrochloric acid is added to dissolve any precipitate at first thrown down, be boiled with a strip of bright copper foil, a dark-grey film of metallic antimony will be deposited on the copper; if the strip of copper be now treated in a manner precisely similar to that described in connection with Reinsch's test for arsenic (*see* page 340), a white sublimate of antimony oxide will be obtained, but differing from the arsenic sublimate in that it is amorphous, and that it is deposited on the sides of the tube much nearer to the copper than the arsenic sublimate, on account of the antimony being less volatile than arsenic.

4. If the operations described under Marsh's test for arsenic (*see* page 341) be repeated, substituting an antimony salt for an arsenical compound, then antimoniuiretted hydrogen (SbH_3) will be evolved; antimoniuiretted hydrogen communicates a livid colour to the burning hydrogen flame, and is decomposed, like arseniuiretted hydrogen, at a low red heat, a black spot of metallic antimony being obtained on a cool porcelain dish or crucible lid introduced for a moment into the flame. As previously mentioned, this antimony spot can be distinguished from the arsenic spot obtained in similar circumstances by being insoluble in solution of chlorinated lime or chlorinated soda, whereas the arsenic spot readily dissolves in either of these solutions.

5. If a piece of platinum foil be put into a solution of an antimony compound, acidulated with hydrochloric acid, and a piece of zinc be then placed in contact both with the platinum and the solution,

the antimony will soon be deposited on the platinum as a brown black stain.

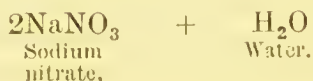
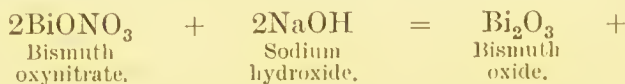
6. If a solid antimony compound be heated on charcoal with sodium carbonate, a brittle metallic globule of antimony is obtained surrounded by a white incrustation.

BISMUTH

Symbol, Bi ; triad ; atomic weight, 208.1 ; specific gravity, 9.75 ; melts at 264°.

Occurrence in nature.—Bismuth occurs in the metallic state in nature, mixed with quartz and other earthy substances ; it is separated by melting it away from these impurities. Bismuth obtained in this way is generally contaminated with variable quantities of the metal arsenic, from which it may be purified by melting it with potassium nitrate, and well stirring the mixture, when the arsenic is oxidised to potassium arseniate. Bismuth is a hard brittle metal with a reddish tinge. Hydrochloric and sulphuric acids do not act upon it in the cold. Nitric acid dissolves it readily. It forms various fusible alloys, the most useful of which is *Wood's metal*, which contains 4 parts by weight of bismuth, 2 of lead, 1 of tin, and 1 of cadmium ; it melts at 61°, and is very useful for taking casts ; it is quite hard when cold.

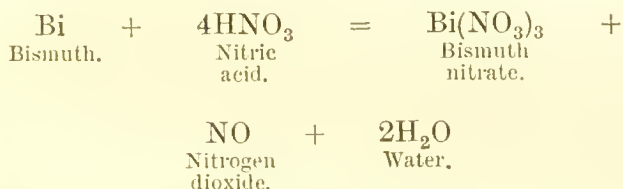
Bismuth oxide (Bi_2O_3) is prepared by boiling bismuth oxynitrate with solution of caustic soda ; it is a yellow powder.



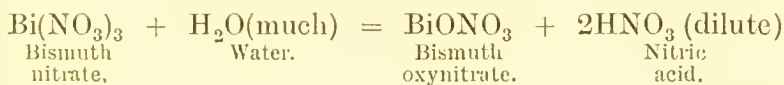
Ordinary impurities.—Chloride, sulphate, carbonate, nitrate ; arsenic and other metals.

BISMUTH SALTS

Bismuth nitrate $[\text{Bi}(\text{NO}_3)_3]$ is prepared by the action of strong nitric acid on bismuth.



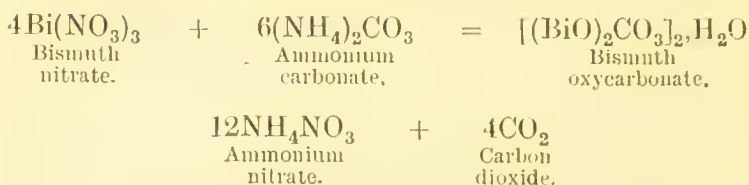
Bismuth oxynitrate $(\text{BiONO}_3, 5\text{H}_2\text{O})$. — This compound is derived from bismuth nitrate, by the displacement of two univalent nitric radicles by the dyad oxygen ; it is prepared by pouring bismuth nitrate into water, when it is thrown down as a white precipitate.



It is largely used in medicine under the name of subnitrate of bismuth (*bismuthi subnitratis*) ; it is also employed as a cosmetic or face-powder under the name of *Pearl white* (Blanc de Perle).

Ordinary impurities.—Chloride, sulphate, carbonate, phosphate ; arsenic and other metals.

Bismuth oxycarbonate $[(\text{BiO})_2\text{CO}_3]_2, \text{H}_2\text{O}$. — This compound may be regarded as a *basic* salt (see page 66), resulting from the interaction of the trivalent base, bismuth hydroxide, $\text{Bi}(\text{OH})_3$, and the dibasic carbonic acid, H_2CO_3 . It is prepared by pouring bismuth nitrate into a solution of ammonium carbonate.



This compound is also extensively used in medicine under the name of carbonate of bismuth (*Bismuthi carbonas*).

Description.—Heavy, cream-coloured powder, insoluble in water.

Ordinary impurities.—Chloride, sulphate, nitrate; arsenic and other metals.

Tests for Bismuth

1. If a solution of a normal salt of bismuth is concentrated and then poured into an excess of water, a white insoluble basic salt is precipitated.

2. Hydrochloric acid added to a neutral solution of a bismuth salt gives a white precipitate of bismuth oxychloride, soluble in excess of hydrochloric acid. The only other metal yielding a white precipitate with hydrochloric acid, soluble in excess of the acid, is antimony; the two metals can be readily distinguished by the different colours of their sulphides, as precipitated by sulphuretted hydrogen, the sulphide of bismuth being black and the sulphide of antimony orange-red. The oxychloride of antimony is also soluble in tartaric acid, in which the corresponding bismuth compound is insoluble.

3. Sulphuretted hydrogen gives with bismuth salts a brownish-black precipitate of bismuth sulphide. The precipitate is insoluble in solution of ammonium sulphide, but is soluble in dilute nitric acid.

4. If a solid compound of bismuth be heated on charcoal with sodium carbonate, a brittle bead

of bismuth is obtained surrounded with an orange incrustation.

As already mentioned (page 236), arsenic, antimony, and bismuth belong to the same chemical family as nitrogen and phosphorus. To the illustrations of this, which were then given, we may now add others. Phosphorus, arsenic, antimony, bismuth are all *brittle* solids. Allotropic varieties are known of the first three. These three also betray their family resemblance in analytical reactions. To draw safe conclusions from the result of an "arsenic test" it is often necessary to be sure of the absence of phosphorus or antimony. Arsenites and phosphates give similar precipitates both with silver nitrate and with barium chloride. The arsenates crystallise in the same form as the corresponding phosphates, and both these salts give a crystalline precipitate with magnesium sulphate in the presence of ammonium salts.

CHAPTER VII

CHROMIUM—MANGANESE—IRON—COBALT— NICKEL

Chromium—Chromium Compounds—Tests for Chromium—Manganese—Manganese Compounds—Tests for Manganese—Iron—Natural Compounds of Iron—Preparation and Properties of the Metal—Cast Iron—Wrought Iron—Steel—Ferrous and Ferric Salts—Tests for Iron—Distinguishing Tests between Ferrous and Ferric Salts—Cobalt—Nickel.

CHROMIUM

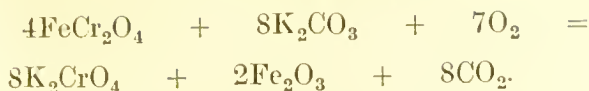
Symbol, Cr. ; hexad ; atomic weight, 52.2 ; specific gravity, 6.92.

THE principal compound of chromium occurring in nature is *chrome iron ore* ($\text{FeO}, \text{Cr}_2\text{O}_3$).

Chromium is a white, very infusible metal, prepared by heating the green oxide of chromium (Cr_2O_3) with carbon in the electric furnace, or by igniting a mixture of the same oxide with finely divided aluminium.

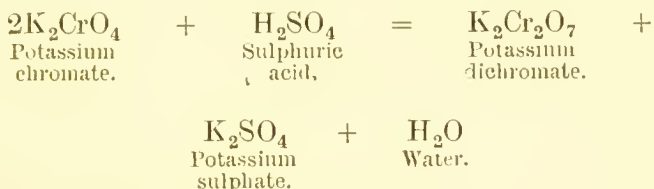


Potassium chromate (K_2CrO_4).—This compound, known also as *yellow chromate of potash*, is prepared from chrome iron ore by fusing it with potassium carbonate and adding oxygen from nitre, air, or other source; ferric oxide and potassium chromate result, the latter being dissolved out by boiling the fused mass with water.

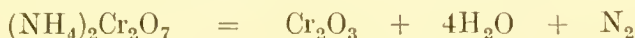


Potassium dichromate ($\text{K}_2\text{CrO}_4, \text{CrO}_3$). —

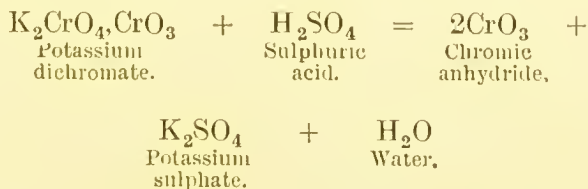
This is more commonly called *bichromate of potash*, or, on account of its colour, *red chromate of potash*. It is prepared by adding to a solution of potassium chromate the theoretical quantity of sulphuric acid, when the dichromate crystallises out on cooling, in hard, deep-red crystals.



Chromic oxide (Cr_2O_3). — Green oxide of chromium may be prepared by strongly heating ammonium dichromate.



Chromic anhydride (CrO_3). — Red oxide of chromium is obtained by mixing together two volumes of a saturated solution of potassium dichromate and three volumes of strong sulphuric acid; as the mixture cools, the chromic anhydride crystallises out in long slender needles of a bright crimson colour.



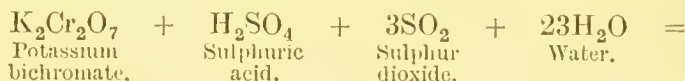
Chromic anhydride is used as a powerful caustic under the name of chromic acid (*acidum chromicum*);

it is the anhydride of chromic acid, into which it is converted by dissolving in water.



Solutions of chromic acid and potassium bichromate are much used for hardening tissues for histological purposes. A solution of gelatin containing 10 per cent. of potassium bichromate becomes, after exposure to light, insoluble in hot water.

Chrome alum $[\text{Cr}_2(\text{SO}_4)_3, \text{K}_2\text{SO}_4, 24\text{H}_2\text{O}]$. — This is prepared by heating potassium dichromate with sulphuric acid in presence of some reducing agent such as alcohol, sulphur dioxide, hydrogen sulphide, nascent hydrogen, etc.



Tests for Chromium

Neutral solutions of chromates give with solution of silver nitrate a rich-red precipitate of silver chromate; the precipitate is soluble in ammonia solution and also in dilute nitric acid.

The same solutions give with lead acetate solution, or with barium chloride solution, a yellow precipitate, insoluble in dilute acetic acid.

If a chromium salt be fused with sodium carbonate and potassium nitrate on a piece of platinum foil, the yellow sodium chromate is formed; on dissolving this in boiling water, and acidifying the solution with acetic acid, a yellow precipitate (lead chromate) will be obtained on the addition of lead acetate.

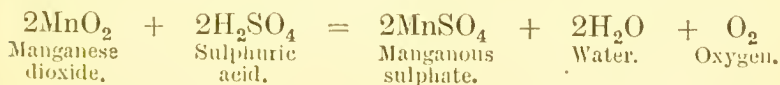
If a solid chromium compound be fused into a borax bead, the latter is coloured green.

MANGANESE

Symbol, Mn ; *heptad* ; *atomic weight*, 55.

The chief natural compound of manganese is the *black oxide of manganese* or *pyrolusite* (MnO_2). Manganese exerts its full valency as a heptad in potassium permanganate, KMnO_4 , which is isomorphous with potassium perchlorate, KClO_4 , in which chlorine is also a heptad (*see* page 64). In potassium manganate (K_2MnO_4), however, the element is hexad, like sulphur in K_2SO_4 and chromium in K_2CrO_4 . In the black peroxide, MnO_2 , the element is only using the valency of a tetrad, whilst in manganous sulphate (MnSO_4) and manganous chloride it acts as a dyad only. The metal is added to Bessemer steel to improve its quality.

Manganous sulphate ($\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$).—When manganese dioxide is heated with strong sulphuric acid, oxygen is evolved and manganous sulphate produced.



Manganous chloride (MnCl_2).—This compound is obtained as a by-product in the preparation of chlorine from manganese dioxide and hydrochloric acid (*see* page 171). The manganous salts have a pale rose tint.

Potassium manganate and permanganate.—The latter of these compounds is the most important manganese preparation, from the medical point of view. (For their preparation and properties, *see* pages 269, 270.)

Tests for Manganese

In a neutral solution of a manganous salt—

1. Ammonium sulphide produces a flesh-coloured precipitate of manganous sulphide.

2. Solution of ammonia produces a white precipitate of manganous hydrate, which darkens on exposure to the air, owing to absorption of oxygen and conversion into the black oxide of manganese.

3. If a manganese compound be fused with sodium carbonate and potassium nitrate on a piece of platinum foil, the green sodium manganate is obtained; if this be boiled with water, it gives a red solution, owing to the conversion of the manganate into the permanganate.

4. If a manganese compound be fused into a borax bead, the latter is coloured amethyst in the outer, but remains colourless in the inner, flame.

IRON

Symbol, Fe; triad (but acts as dyad in ferrous compounds); atomic weight, 56; specific gravity, 7.8.

Natural compounds of iron.—1. The important ore *red hæmatite* consists of ferric oxide (Fe_2O_3); *brown hæmatite* is a ferric oxyhydrate. 2. *Magnetic iron ore* or *loadstone* consists of ferros-ferric oxide (FeO , Fe_2O_3). 3. *Spathic iron ore* is an impure ferrous carbonate (FeCO_3); it is found in England mixed with clay, and constitutes *clay iron-stone*. 4. Iron occurs to a small extent in the free state in nature in the form of meteorites, which are masses of iron that have fallen on to the earth's surface from extra-terrestrial space. 5. Iron also occurs largely in iron pyrites (FeS_2), but this is not used as an iron ore.

Before studying the preparation of metallic iron

from its ores it will be advantageous to state shortly the enormous influence that comparatively small doses of carbon exert on the physical and chemical properties of iron.

Wrought iron contains less than 0.2 per cent. of carbon; it is extremely malleable, infusible in any ordinary furnace, very tough, and when made white hot it becomes pasty, so that two pieces brought together while hot, and hammered, can be *welded* together.

Steel contains from 0.3 to 1.4 per cent. of carbon, is malleable, can be fused in a furnace with a good draught, and can be welded; but its most important property is that it can be *tempered*—i.e. its hardness can be altered by the rate at which it is cooled; if, for instance, when red hot it is plunged into cold water, it is hard enough to scratch glass, but is very brittle; if, on the other hand, it be allowed to cool gradually it is almost as soft and malleable as wrought iron.

Cast iron contains from 2 to 5 per cent. of carbon, it is comparatively hard and brittle, easily fusible, and cannot be welded. If it is cooled quickly its fracture is usually white; if it is cooled slowly some of the carbon separates as grey particles of graphite.

Cast iron is obtained by first smelting or roasting the iron ore in air, in order completely to convert it into ferric oxide, and then reducing the oxide to the metallic state by strongly heating with coke or coal in presence of some limestone; this reduction of the ferric oxide requires a very high temperature, and is carried out in the *blast-furnace* (Fig. 37). This furnace is constructed of very solid masonry lined with firebricks, and reaches from 60 to 80 feet in height; it is fed from the top, alternate layers of roasted iron ore mixed with limestone and coke or coal being shot in from trucks.

The furnace is supplied at the lower part with a powerful blast of air forced through pipes called

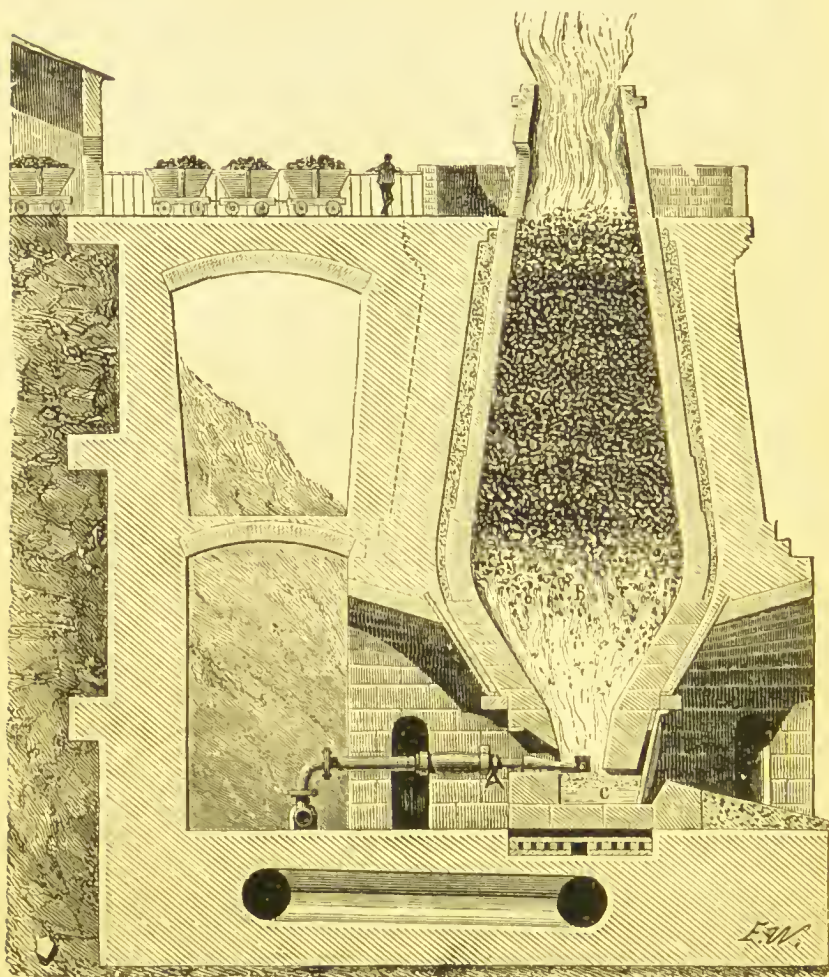
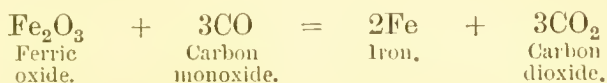


Fig. 37.—Section of a blast furnace.

tuyères, one of which is shown in the figure at A ; this air is heated previously to being forced into the furnace, the hot gases from the top of the furnace being employed for the purpose ; to prevent the escape of these gases a cap or hood (not shown in

the figure) is placed over the top of the furnace, the gases being conducted by pipes issuing from near the top of the furnace to a chamber through which the pipes conveying the blast of air circulate; by thus using a blast of heated air a much higher temperature is obtained within the furnace. Some of the carbon burns to form carbon dioxide, which with the remaining red-hot carbon produces carbon monoxide, a very powerful reducing agent, and this gas in its passage over the lumps of heated ferric oxide abstracts the oxygen, forming carbon dioxide, and setting free the metal.



The metal iron, in a soft or spongy condition, gradually settles down towards the bottom of the furnace; when it arrives at the hottest part (B in figure), it takes up from 4 to 5 per cent. of the carbon, melts, and then accumulates in the molten state at the bottom of the furnace (C in figure). The function of the limestone is to combine with impurities originally present in the iron ore (mainly silica and phosphates). In this way it forms a fusible silicate of calcium and alumina, or *slag*, and so prevents the silica and phosphates from interfering with the running together of the melted cast iron. This fusible slag also trickles down towards the base of the furnace, but being much lighter than the molten iron, it floats on the top of it, and flows out through a suitable opening in the side of the furnace. At the base of the furnace the molten cast iron is run out from time to time through an opening which is temporarily blocked up with clay; it is run into channels made in sand, and solidifies into bars technically known as *pig-iron*. If cast iron be

treated with diluted sulphuric or hydrochloric acid, the iron will dissolve in the acid with evolution of hydrogen, and the minute crystals of graphite will be left insoluble, while the carbon combined with the iron, as carbide of iron, will unite with some of the escaping hydrogen and form hydrocarbon gases possessing a peculiar and rather disagreeable odour.

Wrought iron is prepared by burning out the carbon from cast iron, which can be effected by melting the cast iron in the bed of a reverberatory furnace, and then, while a current of hot air is passing over the surface of the molten iron, well stirring or *puddling* it so as freely to expose it to the action of the oxygen; in this way the carbon of the cast iron is gradually burnt out, and as the less easily fusible wrought iron is produced, the metal assumes a pasty condition. As the wrought iron is formed it is taken out in lumps, which after hammering are rolled out.

During this process, known as the “puddling process,” the iron loses sulphur and phosphorus as well as carbon, and so is much improved in toughness.

Steel is intermediate in composition between cast iron and wrought iron, and it is obvious that it may be prepared (1) by abstracting part of the carbon from cast iron, till the percentage of carbon is reduced sufficiently; (2) by the addition of carbon to wrought iron, so as to raise the percentage; (3) by mixing cast iron and wrought iron in such proportions that the mixture shall contain 0·3 to 1·4 per cent. of carbon. These are the three methods actually employed, the first being known as the Bessemer process, the second the old or Cementation process, and the third the Siemens-Martin process.

1. *Bessemer process*.—This consists in burning out the carbon in cast iron, by passing a current of

air through melted cast iron. The Bessemer converter is a large egg-shaped vessel lined with powdered flint and provided with openings at the base, through which a current of air can be forced; molten cast iron is run in, and the air passed through it, the oxygen of the air rapidly burning away most of the carbon; enough "spiegeleisen" (a variety of cast iron containing manganese) is then added to impart the necessary amount of carbon and manganese, a small quantity of the latter element notably improving the quality of the steel. It is almost impossible to estimate the value of this process: it has practically given us a new material, in cheap steel. In 1856, when the Bessemer process was first used, steel cost £50 a ton, now it can be made for £6 a ton. The original Bessemer process suffered from the defect that as the lining of the converter was silica, an *acid* oxide, all the phosphorus in the cast iron passed into the steel, necessitating, therefore, the use of a cast iron free from phosphorus. This defect was completely overcome by Thomas and Gilchrist, who substituted a *basic* oxide (a mixture of lime and magnesia) for the powdered flints. The phosphorus combines with the basic lining and passes into the slag, which is sold as a manure, leaving the steel free from this fatal impurity.

2. *Cementation process*.—In this, the old process for producing steel, carbon is added to wrought iron. It is carried out by embedding bars of wrought iron in charcoal powder, and then heating to bright redness for some days; carbon is gradually taken up by the wrought iron, probably by some process of diffusion, and steel is produced—the product is known as *blister steel*; this is melted to distribute the carbon more equally and is then known as *cast steel*.

3. *Siemens-Martin process*.—This consists in fusing

cast iron, and then adding to it wrought iron and a small quantity of "spiegeleisen," until the percentage of carbon is brought from 0.3 to 1.4.

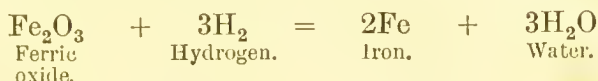
Properties of the metal iron.—*Cast iron* has a grey colour, and a crystalline or granular structure; as previously mentioned, its carbon exists partly in the form of minute crystals of graphite disseminated through the mass of the iron, and partly in union with some of the iron as a carbide of iron. Cast iron melts at a lower temperature than any other form of iron.

Wrought iron is fibrous in structure, and therefore much stronger than the crystalline or granular cast iron, but the fibrous texture is apt to undergo a change into the granular condition when exposed to long-continued vibration. All forms of iron are rendered extremely brittle by the presence of silicon, sulphur: or phosphorus, hence the importance of removing these impurities in the slag during the preparation of iron in the blast furnace. Pieces of wrought iron can be welded or joined together by bringing their clean surfaces in contact at a red heat and then hammering them; to clean their surfaces from the film of oxide of iron, which is produced by the action of the air on the heated iron, the blacksmith uses some sand as a flux previous to hammering; the silica uniting with the oxide of iron forms a fusible silicate of iron, which is squeezed out during the process of hammering, and so allows the absolutely clean metallic surfaces to come into contact and unite.

Steel is of a pale-grey colour, and capable of taking a high polish; it is finely granular, not fibrous in structure. *Hard steel* is prepared by heating steel to redness, and then rapidly cooling it by immersion in water; it then becomes exceedingly brittle. To toughen or *temper* steel, it is gently re-heated, and

when the desired temperature is reached, again rapidly cooled.

Reduced iron is pure iron in the form of powder, obtained by passing a stream of hydrogen over heated ferrie oxide; the oxygen is abstracted as water, and the iron is left in a finely divided state. It contains about 75 per cent. of metallie iron; the rest is chiefly oxide.



All kinds of iron are magnetic—that is, capable of being attracted to and picked up by a magnet, and also capable of being magnetised; soft iron readily becomes magnetised when in contact with a magnet, but loses its magnetism when withdrawn from the magnet, whereas hard steel becomes magnetised very slowly, but when once magnetised retains its magnetism for a long period.

Iron remains unchanged in dry air or oxygen at ordinary temperatures, but in moist air it readily unites with oxygen and moisture, forming reddish-brown *rust*, a ferrie oxyhydrate. The carbon dioxide always present in the air has been credited at different times with a more or less important share in promoting this action. The exact nature and value of this share is still uncertain. At a red-heat, iron is more rapidly oxidised than by moist air at ordinary temperatures, as is well seen in the production of the forge-seales that collect around the blacksmith's anvil, which consist of the black magnetic oxide of iron (Fe_3O_4).

Barff's process for the prevention of rusting of iron consists in coating the iron article with a film of the hard black magnetic oxide, which effectually prevents further oxidation in damp air; to effect

this a current of steam is passed for a few minutes over the iron article heated to about 650° .



Action of acids on iron (see page 74).—Dilute sulphuric acid acts on iron, forming ferrous sulphate and evolving hydrogen.



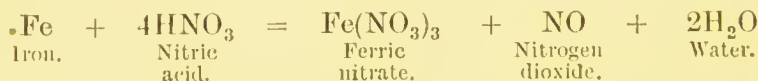
Strong sulphuric acid, with heat, also acts on iron, but in this case with evolution of sulphur dioxide.



Hydrochloric acid acts on iron, forming ferrous chloride, and evolving hydrogen.



Hot dilute nitric acid attacks iron, forming ferric nitrate, and evolving nitrogen dioxide.



In contact with the concentrated acid iron assumes a curious “passive” state, in which it seems to be immune to the acid.

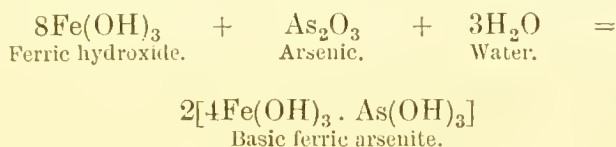
Ferrous oxide (FeO) is a black powder obtained by heating ferrous oxalate to 150° in the absence of air.

Ferrous hydroxide $[\text{Fe}(\text{OH})_2]$ is obtained by precipitating a solution of ferrous sulphate with KHO in the absence of air. It is a white substance, very rapidly absorbing oxygen, turning dark green and then gradually rusty brown.

Ferric hydroxide $[\text{Fe}(\text{OH})_3]$ is prepared by precipitating a solution of ferric sulphate or ferric chloride with an alkali, caustic soda being generally employed for the sake of cheapness.



Freshly precipitated ferric hydrate is used as an antidote in cases of poisoning by arsenic, the reaction between the ferric hydrate and the arsenic resulting in the formation of an insoluble ferric arsenite.



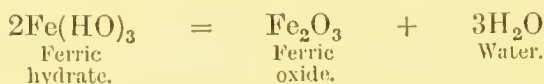
Freshly precipitated ferric hydrate dissolves in a solution of perchloride of iron, forming a dark-red solution of basic chloride of iron; if this solution be placed in a dialyser, the greater proportion of the hydrochloric acid of this basic chloride passes through the dialyser, leaving a still more basic chloride of iron.

Freshly precipitated ferric hydrate is also used in the preparation of the iron scale compounds, which are uncrystallisable bodies obtained in the solid form by the evaporation of their solutions to a syrup, and then allowing the syrup to dry in scales. Citrate of iron and ammonium (*ferri et ammonii citras*) is prepared by dissolving ferric hydrate in a solution of citric acid, adding ammonia, evaporating to a

syrup, and drying in scales; it is a double citrate of iron and ammonium. Citrate of iron and quinine (*ferri et quiniae citras*) is prepared by dissolving ferric hydrate and quinine in a solution of citric acid, adding ammonia (not in excess, or the quinine would be precipitated), evaporating to a syrup, and drying in scales; it is a triple citrate of iron, quinine, and ammonium. Tartarated iron (*ferrum tartaratum*) is prepared by dissolving ferric hydrate in a solution of potassium acid tartrate, evaporating to a syrup, and drying in scales; it is a double tartrate of iron and potassium.

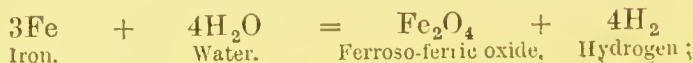
Alkaline bicarbonates, which are incompatible with most iron preparations, can be prescribed with citrate of iron and ammonium, and with tartarated iron, without the iron being precipitated; they would not be compatible with citrate of iron and quinine, as the quinine would be thrown down by alkaline carbonates.

Ferric oxide (Fe_2O_3) is prepared by further heating ferric hydrate.

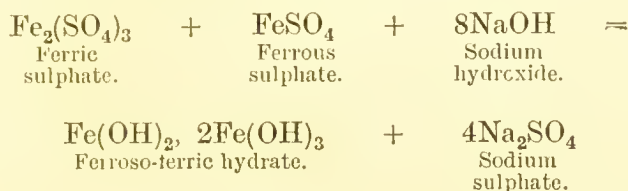


It may also be prepared by roasting crystals of ferrous sulphate until fumes of the Nordhausen sulphuric acid cease to be evolved. This variety of ferric oxide passes under the names of *red oxide of iron*, *mineral rouge*, *Venetian red*, *colcothar*, and *crocus*; it is used for polishing.

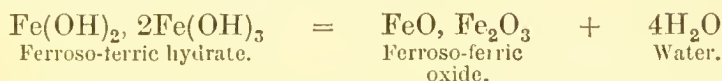
Ferroso-ferric oxide ($\text{FeO}, \text{Fe}_2\text{O}_3$) is also known as black oxide of iron and magnetic oxide of iron. It may be prepared (1) by passing steam over red-hot iron—



(2) by precipitating a mixed solution of ferric and ferrous sulphates with caustic soda, when the black ferroso-ferric hydrate is thrown down.



This when heated in a closed vessel loses water and yields the ferroso-ferric oxide.



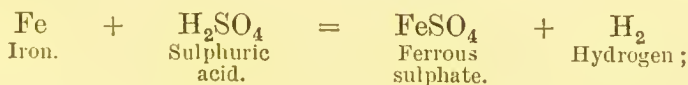
(3) The black *forge-scales*, which collect around the blacksmith's anvil, consist of the ferroso-ferric oxide.

IRON SALTS

Two classes of iron salts exist, the ferrous and the ferric. In the ferrous salts the iron is only exerting part of its valency, and acting as a dyad ; whereas in ferric salts it acts as a triad.

FERROUS SALTS

Ferrous sulphate ($\text{FeSO}_4, 7\text{H}_2\text{O}$).—This salt is also known as *protosulphate of iron*, *green vitriol*, *copperas*, and *green copperas*. It is prepared (1) by the action of dilute sulphuric acid on iron (*see page 577*)—



(2) by the action of dilute sulphuric acid on ferrous sulphide, this being the ordinary method

employed for the preparation of sulphuretted hydrogen—



(3) by gently roasting iron pyrites (FeS_2) in the air.

Ordinary ferrous sulphate contains seven molecules of water of crystallisation ($\text{FeSO}_4, 7\text{H}_2\text{O}$). By careful heating, six-sevenths of this water can be expelled, leaving the dried sulphate of iron (*ferrisulphas exsiccatus*) of the composition ($\text{FeSO}_4, \text{H}_2\text{O}$). If further heat be employed, so as to expel this last molecule of water, then the salt is decomposed, ferric oxide being left and Nordhausen sulphuric acid evolved.

If ferrous sulphate be exposed for some time to the air, it loses its green colour and becomes brown, owing to the absorption of oxygen and conversion into basic ferric sulphate.

Ferrous sulphate is very largely employed in the preparation of black writing-ink, the black colour of which is due to tannate of iron in a finely-divided state suspended in weak mucilage, the tannic acid being furnished by an infusion of galls.

Ferrous chloride (FeCl_2).—This salt, also known as protochloride of iron, is prepared by the action of hydrochloric acid on iron.



Ferrous carbonate (FeCO_3) is precipitated by mixing together solutions of ferrous sulphate and potassium carbonate.



Ferrous carbonate is, when first precipitated, of a white colour, but quickly turns green, and ultimately brown, from absorption of oxygen from the air and more or less complete conversion into ferric oxyhydrate.

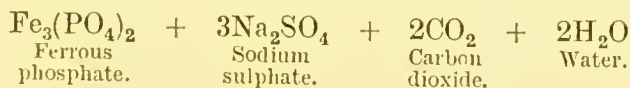
The so-called Griffith's mixture (*mistura ferri composita*) contains green ferrous carbonate in suspension; the absorption of oxygen from the air may be, to a certain extent, prevented by mixing dried ferrous carbonate with sugar (*ferri carbonas saccharata*). Ferrous carbonate is appreciably soluble in water containing carbon dioxide, and is in this way kept in solution in *chalybeate* spring waters. If such a water be exposed to the air for some time, it becomes turbid from the formation and deposition of ferric hydrate.

Ordinary impurity.—Sulphate.

Ferrous sulphide (FeS) is prepared by heating a mixture of iron filings and sulphur, or by rubbing a stick of roll sulphur against a bar of iron at a bright red heat; it is a black solid.

Ferrous iodide (FeI_2) is prepared by warming together iron wire, iodine, and water.

Ferrous phosphate [$\text{Fe}_3(\text{PO}_4)_2$] is prepared by mixing together solutions of ferrous sulphate, sodium phosphate, and sodium bicarbonate.

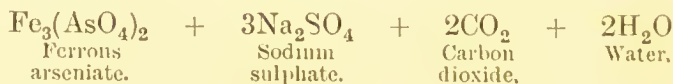
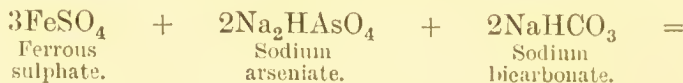


The ferrous phosphate comes down at first as a white precipitate, quickly changing to a bluish colour. The sodium bicarbonate is added to prevent the formation of free sulphuric acid, which

would keep some of the ferrous phosphate in solution.

Ordinary impurities.—Sulphate; arsenic.

Ferrous arseniate [$\text{Fe}_3\text{AsO}_4)_2$] is prepared by mixing together solutions of ferrous sulphate, sodium arseniate, and sodium bicarbonate.

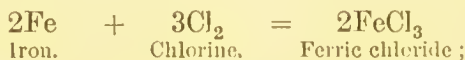


The ferrous arseniate comes down at first as a white precipitate, quickly changing to a greenish colour. The sodium bicarbonate is added for a reason similar to that given in connection with ferrous phosphate.

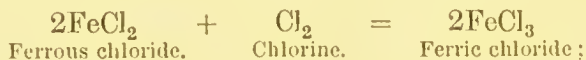
Ordinary impurity.—Sulphate.

FERRIC SALTS

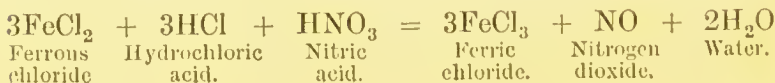
Ferric chloride, or perchloride of iron (FeCl_3).—This may be prepared as black deliquescent plates (1) by passing chlorine over heated iron—



(2) by passing chlorine through a solution of ferrous chloride (on evaporation it forms a yellow solid)—



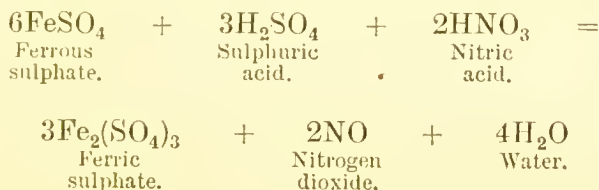
(3) by warming a solution of ferrous chloride with hydrochloric and nitric acids—



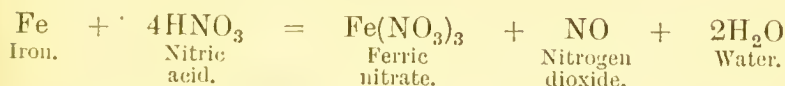
This is the process employed in the preparation of the solution of perchloride of iron used in medicine (*liquor ferri perchloridi*). It really consists in the passage of chlorine into ferrous chloride, since the action of the nitric acid is to oxidise the hydrogen of the hydrochloric acid to water, thus liberating the chlorine, the nitrogen of the nitric acid being evolved as nitric oxide.

Ordinary impurities.—Other metals.

Ferric sulphate, or persulphate of iron [$\text{Fe}_2(\text{SO}_4)_3$], is prepared by warming together a solution of ferrous sulphate with sulphuric and nitric acids.



Ferric nitrate, or pernitrates of iron [$\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$], is prepared by the action of hot dilute nitric acid on iron.

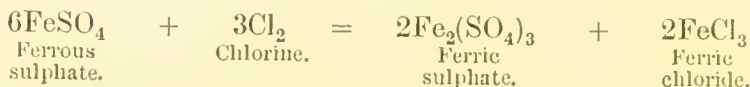
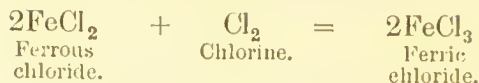


Ordinary impurities.—Other metals.

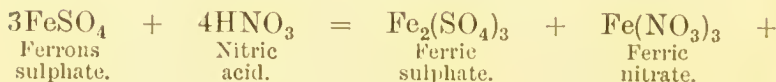
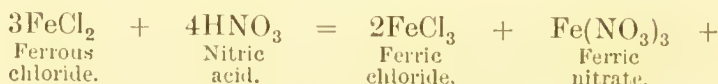
Ferric acetate, or peracetate of iron [$\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$], is prepared by dissolving freshly precipitated ferric hydrate in glacial acetic acid.

Iron and cyanogen compounds. (*See Organic Chemistry, Chapter IX.*)

General methods of raising ferrous salts to the ferric state.—This conversion is really a process of *oxidation* (*see page 76*), and the following are therefore particular examples of oxidation: 1. The passage of chlorine gas through a solution of a ferrous salt raises it to the ferric state—

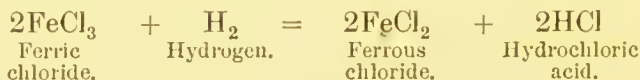


2. Nitric acid with heat will raise any ferrous salt to the ferric state, thus :



3. Long-continued exposure to air will convert most, and heating in the air will convert all, ferrous salts into ferric salts.

General methods of reducing ferric salts to the ferrous state.—These are really particular examples of reduction (*see* page 76). 1. If to a solution of a ferric salt some zinc be added, and then sufficient hydrochloric acid to act on the zinc and liberate hydrogen, the nascent hydrogen will reduce the ferric salt to the ferrous state.



2. If sulphuretted hydrogen be passed through a solution of a ferric salt, the latter will be reduced to the ferrous state, sulphur being thrown down.



3. If to a solution of a ferrie salt, solution of stannous chloride be added, the former will be reduced to the ferrous state, the latter being raised to the stannic state.



Tests for iron in solutions of a ferrous salt

1. Ammonium sulphide gives a black precipitate of ferrous sulphide.

2. Sulphuretted hydrogen gives no precipitate with a ferrous salt in *acid* solutions. This negative reaction is of value in the separation from iron of metals precipitated by sulphuretted hydrogen in presence of free hydrochloric acid.

3. Potassium ferrocyanide (K_4FeCy_6) gives with ferrous salts a precipitate, at first almost white, but rapidly changing to a light-blue colour, owing to absorption of oxygen from the air. The original precipitate is a double ferrocyanide of iron in the ferrous state and potassium ($\text{FeK}_2\text{FeCy}_6$).

4. Potassium ferricyanide (K_3FeCy_6) gives with ferrous salts a dark blue precipitate (KFe_2Cy_6), sometimes, though erroneously, called Turnbull's blue ($\text{Fe}_3\text{Fe}_2\text{Cy}_{12}$).

5. Potassium sulphocyanide gives no colour with ferrous salts, provided that they are quite free from ferrie salts.

6. Alkalies, such as ammonia, potash, and soda, partially precipitate ferrous salts as ferrous hydrate, the precipitate being white at first, but rapidly turning to a greenish colour from absorption of oxygen from the air, and then slowly becoming rusty brown.

Tests for iron in solutions of a ferric salt

1. Ammonium sulphide reduces a ferric salt to the ferrous state, producing a mixed precipitate of the black ferrous sulphide and sulphur.

2. Sulphuretted hydrogen passed through a solution of a ferric salt reduces it to the ferrous state, sulphur being precipitated.

3. Potassium ferrocyanide (K_4FeCy_6) gives a dark-blue precipitate (KFe_2Cy_6), sometimes, though erroneously, called Prussian blue [$Fe_4(FeCy_6)_3$].

4. Potassium ferricyanide gives with a solution of a ferric salt an olive colour, no precipitate being produced.

5. Potassium sulphocyanide gives with solutions of ferric salts a deep blood-red colour, due to the formation of the soluble ferric sulphocyanide.

6. The alkalis, ammonia, potash, and soda, precipitate from ferric solutions the foxy-red ferric hydrate.

Ferrous solutions are generally colourless to pale green; ferric solutions are generally pale-yellow to red in colour.

DISTINGUISHING TESTS BETWEEN FERROUS AND FERRIC SALTS

	FERROUS SALTS	FERRIC SALTS
Potassium ferro- cyanide	Light blue precip.	Dark blue precip.
Potassium ferri- cyanide	Dark blue precip.	No precip.; olive colour produced.
Potassium sulpho- cyanide	No change of colour <i>if the ferrous salt is pure.</i>	Dark blood-red colour.
Alkalies	Green precip., turn- ing rusty-brown on surface.	Foxy-red precipi- tate.

COBALT AND NICKEL

Occur in nature usually in combination with arsenic and sulphur, from which the metals are extracted by a somewhat complex process. Both metals are hard, magnetic, malleable, and white, and have a specific gravity of about 8.8. They melt at very high temperatures (nickel 1484° ; cobalt 1530°), and are both used for plating iron, brass, etc.

The *cobalt salts*, when hydrated, are usually pink in colour, but when rendered anhydrous by heat they become blue.

The most common salt is the nitrate $[\text{Co}(\text{NO}_3)_2 + 6\text{H}_2\text{O}]$; it is used as a test, in the dry way, for aluminium, zinc, and magnesium compounds.

Nickel has become recently of great importance in connection with the steel industry, since steel, by the addition of about 5 per cent. of nickel, has its tensile strength increased about one-half. Very valuable deposits of nickel sulphide were found in Canada during the construction of the Canadian Pacific Railway. Much nickel is used for making German silver, which is brass (copper and zinc) alloyed with 10 to 20 per cent. of nickel. The nickel salts are usually green.

Cobalt compounds give a blue colour to a borax bead and to glass, nickel compounds give a smoke-coloured borax bead.

Nickel forms a colourless volatile liquid with carbon monoxide $\text{Ni}(\text{CO})_4$. The corresponding cobalt compound is known, and from this, $\text{Co}(\text{CO})_3$ has also quite recently been obtained, by the action of heat (*Proc. Chem. Soc.*, 1910, page 77).

CHAPTER VIII

COPPER—SILVER—GOLD—PLATINUM

Copper—Natural Compounds of Copper—Preparation and Properties of Metallic Copper—Copper Salts—Tests for Copper. Silver: Extraction and Properties of Metallic Silver—Silver Salts—Tests for Silver. Gold. Platinum. The Four Metals Compared.

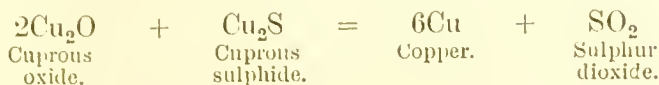
COPPER

Symbol, Cu ; *dyad* ; *atomic weight*, 63.6 ; *specific gravity*, 8.9 ; *melts*, 1085°.

Natural compounds of copper.—1. The commonest copper ore is *copper pyrites*, a double sulphide of copper and iron (CuFeS_2), containing in addition some sulphide of arsenic. 2. *Cuprite* or *red copper ore* consists of cuprous oxide (Cu_2O). 3. *Malachite* is a mixed carbonate and hydroxide of copper [CuCO_3 , $\text{Cu}(\text{HO})_2$]. 4. The metal copper is found to a certain extent free in nature, occurring especially in North America.

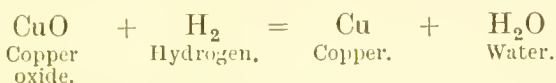
Preparation of the metal copper.—The separation of metallic copper from copper pyrites is a lengthy and complicated process. To describe it briefly: the copper ore is roasted; the temperature is then raised till the ore fuses; the two chief products are cuprous sulphide and silicate of iron; the silicate of iron is separated; by repeating the roasting and fusing, all the iron is removed as silicate. The nearly pure cuprous sulphide is now carefully roasted until two-thirds are converted into oxide. The tempera-

ture is then raised, and the following reaction takes place :



The copper is remelted and stirred up with a pole of wood to reduce any oxide which may be present.

Chemically pure copper may be obtained by passing hydrogen over copper oxide raised to a red heat, or by electrolysis.



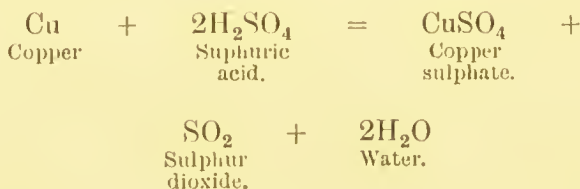
Properties of the metal copper.—Copper is one of the few metals possessing a distinctive colour—it is red ; it is a very malleable and ductile metal, and is an extremely good conductor of both heat and electricity : hence its employment for lightning conductors, etc. Copper remains unchanged in dry air, but in moist air it becomes gradually covered with a green layer of a basic copper carbonate, frequently mistaken for verdigris (oxyacetate of copper). Water can be boiled in copper vessels without attacking them, but a solution of common salt slowly attacks copper, forming a green oxychloride of copper, and vinegar still more readily acts on copper vessels, forming verdigris (oxyacetate of copper) ; hence the danger of using copper vessels for culinary purposes, the copper salts produced by the action of common salt and vinegar being poisonous. Copper, heated to redness in the air, readily oxidises, forming the black copper oxide (CuO). The metal copper is deposited from its solutions by either iron or zinc, and it is also deposited at the kathode when an electric current is passed through

a solution of copper sulphate, a process employed in producing electrotypes or copies of objects in copper.

Copper enters into the formation of several very useful alloys. *Brass* contains about 70 parts of copper to 30 parts of zinc; a larger proportion of zinc yields an alloy of a pale yellow colour, known as *Muntz metal*, largely used for covering wooden ships; by increasing the amount of copper, and adding a little tin, *Dutch metal* is obtained. *Bronze*, *gun-metal*, and *bell-metal* are alloys of copper and tin containing from 80 to 90 per cent. of copper; *speculum metal* is a hard white alloy of 2 parts of copper to 1 part of tin with a little arsenic; it is capable of taking a high polish, and is used for the mirrors of reflecting telescopes. *German silver* or *nickel silver* is an alloy of copper, zinc, and nickel; all silver articles and silver coins contain some copper, in order to render the silver harder; *aluminium bronze* or *aluminium gold* is an alloy of copper and aluminium.

Action of acids on copper (see page 74).

—Dilute sulphuric acid has no action on the metal copper. Strong sulphuric acid with heat readily acts on copper, forming the sulphate and evolving sulphur dioxide gas.

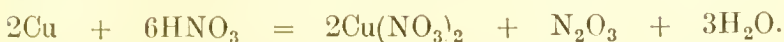


Warm, dilute nitric acid readily acts on copper, forming copper nitrate, with evolution of nitrogen dioxide.





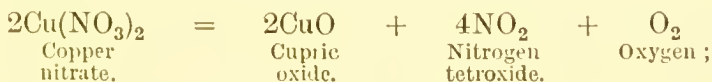
The concentrated acid causes evolution of some N_2O_3 —



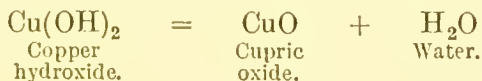
Hydrochloric acid has no action on copper.

Cuprous oxide (Cu_2O).—Red oxide of copper is best prepared by boiling a mixed solution of copper sulphate, grape sugar, and caustic potash or soda; in the absence of the grape sugar, black cupric oxide (CuO) would be thrown down, but the grape sugar, by abstracting one-half of the oxygen from the cupric oxide, reduces it to the red cuprous oxide, which is precipitated. This constitutes a test for sugar in diabetic urine.

Cupric oxide (CuO).—Black copper oxide may be obtained (1) by roasting metallic copper in air, (2) by heating copper nitrate—



(3) by adding caustic soda to a solution of copper sulphate to precipitate the light-blue copper hydroxide $[\text{Cu}(\text{OH})_2]$, and then boiling the liquid, when the hydroxide decomposes into cupric oxide and water.



COPPER SALTS

Copper forms two classes of compounds, *cupric* and *cuprous*.

Cupric chloride (CuCl_2) is obtained as a brown powder by burning metallic copper in chlorine,

or as a green solution by dissolving the carbonate in hydrochloric acid.

Cuprous chloride (Cu_2Cl_2 , or CuCl) is obtained by boiling cupric chloride with hydrochloric acid and copper turnings and pouring the solution into water, when it is thrown down as a white precipitate.

Copper sulphate ($\text{CuSO}_4, 5\text{H}_2\text{O}$). — This, the commonest salt of copper, is also known as *blue vitriol* and *bluestone*. It is prepared (1) by the action of hot strong sulphuric acid on the metal copper, as described in detail on page 577.

(2) by the action of dilute sulphuric acid on cupric oxide—

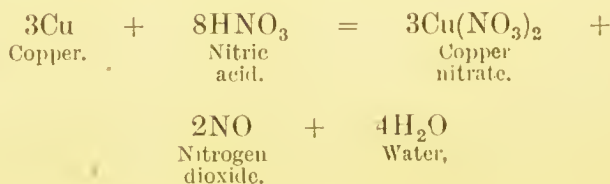


(3) by roasting copper pyrites in the air, by which process it is obtained mixed with sulphate of iron.

Copper sulphate in its crystalline condition contains five molecules of water of crystallisation ($\text{CuSO}_4, 5\text{H}_2\text{O}$); these can be expelled by heat, leaving the anhydrous copper sulphate (CuSO_4), which is of a white colour. If the anhydrous copper sulphate is shaken with liquids containing water, it unites with the water forming the blue crystalline variety, and hence becomes a valuable test for the detection of water in liquids which should, if pure, be free from it, such as absolute alcohol.

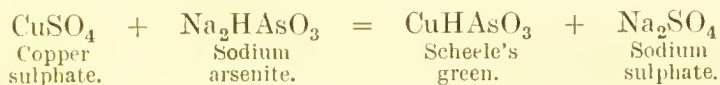
Ordinary impurities.—Iron and other metals.

Copper nitrate [$\text{Cu}(\text{NO}_3)_2, 3\text{H}_2\text{O}$] is prepared by the action of nitric acid on copper.



Copper oxyacetate (verdigris) [$\{(\text{CH}_3.\text{COO})_2\text{Cu}\}_2\text{Cu}(\text{OH})_2$] is prepared by exposing copper to the vapour of acetic acid and the action of the air.

Copper arsenite (Scheele's green) (CuHAsO_3) is prepared by mixing solutions of copper sulphate and sodium arsenite, when it is thrown down as a bright green precipitate.



Scheele's green is very poisonous, mainly on account of the arsenic contained in it; it is a pigment frequently employed in the colouring of wall-papers, book-covers, etc. For the method of detecting it in wall-papers, etc., see page 344.

Tests for Copper

1. Sulphuretted hydrogen gas produces, in solutions of copper salts, a black precipitate of copper sulphide (CuS).

2. Ammonium sulphide produces a similar precipitate of the black copper sulphide.

3. Potassium ferrocyanide, in presence of dilute acetic acid, produces a reddish-brown precipitate of copper ferrocyanide (Cu_2FeCy_6). This is the most delicate test for copper, as an extremely dilute solution of a copper salt is tinted reddish-brown on the addition of potassium ferrocyanide solution.

4. Solution of ammonia gives a light-blue precipitate of copper hydroxide [$\text{Cu}(\text{OH})_2$], readily soluble, in excess of ammonia to a deep blue solution. This is a very delicate test for copper salts. The blue solution contains an ammoniacal copper compound; with copper *sulphate* this would be $\text{Cu}(\text{NH}_3)_4, \text{SO}_4$.

5. Solution of caustic potash or caustic soda produces a light blue precipitate of copper hydroxide, not soluble in excess of the fixed alkali; on boiling the liquid, the light blue precipitate turns black, owing to the decomposition of the copper hydroxide into cupric oxide and water.

6. A piece of bright steel, such as the polished steel blade of a knife, if immersed in an acid solution of a copper salt, becomes in a short time coloured with a reddish deposit of the metal copper upon it. This is a ready and useful test for ascertaining whether a blue liquid contains copper or not.

7. Copper salts give a bluish green colour to the Bunsen flame.

8. When fused into borax, copper salts give in the outer flame a bead which is green when hot and blue when cold; in the inner flame the bead becomes red and opaque.

SILVER

Symbol, Ag; monad; atomic weight, 108; specific gravity, 10.56; melts at 960°.

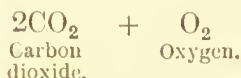
Occurrence in nature.—Silver occurs free in nature; also as *horn silver* (AgCl); *sulphide of silver* (Ag_2S) is frequently contained in other native sulphides, notably in those of lead, copper, and antimony.

Extraction of the metal silver.—The *cupellation process* for extracting silver from lead has already been described in connection with the latter metal (*see* page 324). The *amalgamation process* for the extraction of silver consists in roasting the silver ores with common salt (sodium chloride), by which means silver chloride is formed; the roasted ores are then agitated in barrels with water and scrap iron, the iron abstracting the chlorine from the

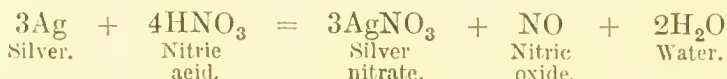
silver chloride to form ferrous chloride, and setting free the metal silver; mercury is then introduced into the barrels and they are again thoroughly agitated, when an amalgam of mercury and silver is formed; this amalgam is removed and heated in retorts, when the mercury distils over, the metal silver being left in the retort. In Mexico the silver ore is ground with water, salt and copper sulphate, and thereby converted into chloride of silver. Mercury is now added and an amalgam of silver formed which is heated as above.



Properties of the metal silver.—Silver is a white, lustrous metal; it is soft, and so malleable that it can be beaten into extremely thin leaves (*silver leaf*). It does not oxidise at any temperature in the air, but in the molten state it possesses the peculiar power of dissolving about 20 times its volume of oxygen from the air; this oxygen is given off when the silver cools and solidifies, producing the phenomenon known as the *spitting* of silver. Sulphuretted hydrogen blackens silver, and hence polished silver articles slowly tarnish when exposed to the air. Pure silver is too soft for use, but by the admixture of a small amount of copper with it, a hard alloy is obtained. Standard silver contains 92·5 per cent. of silver and 7·5 per cent. of copper. To prepare a specimen of pure silver from a coin, dissolve it in nitric acid, and to the green solution add hydrochloric acid, when the silver will be precipitated as silver chloride; this precipitate must be washed till free from copper, and then fused on charcoal with sodium carbonate, when the silver will be obtained as a bright metallic bead.



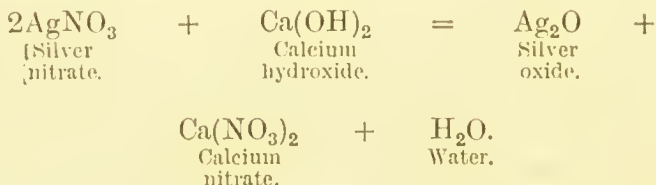
Action of acids on silver (*see* page 74).
 —Hydrochloric acid does not attack silver. Warm dilute nitric acid forms silver nitrate, with evolution of nitric oxide.



Hot strong sulphuric acid acts on silver, forming silver sulphate and evolving sulphur dioxide.



Silver oxide (Ag_2O) is prepared by precipitating a solution of silver nitrate with a solution of potash, soda, or lime; lime-water is preferable on account of its freedom from chlorides.



Silver oxide is a brown powder, which is reduced to the metallic state either by heat or by contact with organic matter; on account of this last-mentioned property it should not be used in medicine combined with an essential oil or other organic substance.

SILVER SALTS

Silver nitrate (AgNO_3) is prepared by the action of nitric acid on silver (page 386). If silver nitrate is carefully melted, and then poured into moulds, it solidifies in the form of sticks, known as *lunar caustic*, a substance frequently employed for external application as a caustic. The blackening produced on the skin after the application of silver nitrate is due to the reduction of the salt to metallic silver. A weaker caustic, known as *mitigated caustic*, is a mixture of silver and potassium nitrates, and is prepared by fusing together one part of silver nitrate with two parts of potassium nitrate.

Description.—Clear, colourless crystals, readily soluble in distilled water.

Ordinary impurities.—Sulphate; other metals.

Silver chloride, bromide and iodide.—These compounds are obtained as precipitates when the corresponding potassium salts are added to a solution of silver nitrate. They are all very sensitive to the action of light, becoming converted probably to an oxysalt after exposure, and this oxysalt, if afterwards treated with a reducing agent, becomes converted into metallic silver. It is on account of their sensitiveness to light that these silver salts are used in the production of photographs. The dry plates now used in photography consist of glass plates covered with a film of silver iodide or bromide suspended in gelatine; these plates are exposed in the camera to the light reflected from the object to be photographed; where the light falls, the silver salt is more or less reduced to a subsalt, according to the intensity of the light. If the exposed plate is now placed in a solution of a reducing agent, such as pyrogallie acid and ammonia, the sub-salt is completely reduced to metallic silver; this is the process known as *develop-*

ing. To preserve this picture, and to prevent the undecomposed silver salt from blackening when exposed to the light, it must now be *fixed*; this process consists in dissolving out the undecomposed bromide or iodide of silver by immersing the plate in a solution of sodium thiosulphate (hyposulphite of soda). (See page 255.)

In this way a *negative* is obtained, showing the bright parts of the object dark and the dark parts light. To *print* an ordinary photograph on to paper, the negative is placed over a sheet of paper prepared with silver chloride, and then exposed to the light.

Silver chloride is white, but rapidly darkens when exposed to daylight. When heated it melts, and, on cooling, forms a dark brown mass like horn, hence it is sometimes called *horn silver*. Silver bromide is whitish in colour, silver iodide is pale yellow, and is insoluble in ammonia.

Tests for Silver

1. Hydrochloric acid produces, in solutions of silver salts, a white, curdy precipitate of silver chloride, insoluble in nitric acid, but soluble in solution of ammonia. The solution contains the compound $\text{Ag}(\text{NH}_3)_2\text{Cl}$.

2. Potassium chromate produces, in a neutral solution of a silver salt, a red precipitate of silver chromate.

3. Sodium phosphate produces, in a neutral solution of a silver salt, a yellow precipitate of silver phosphate.

4. Sulphuretted hydrogen produces a black precipitate of silver sulphide, insoluble in ammonium sulphide, but easily soluble in dilute nitric acid.

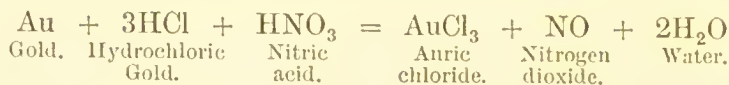
GOLD

Symbol, Au; triad; atomic weight, 197.2; specific gravity, 19.4; melts at 1067°.

Gold occurs in nature in the free state. It is found in masses called nuggets, and also, in a more finely-divided state, in quartz rocks and in alluvial quartz sand which has been deposited by the disintegration of the older rocks. It is extracted by shaking with mercury, or by dissolving it out (1) by chlorine water, or (2) by a weak solution of sodium cyanide. Pure gold is prepared by melting ordinary gold with three parts of silver, and then dissolving out the silver either with nitric acid or by boiling strong sulphuric acid, when the gold is left as a brown powder.

Gold is one of the few metals possessing a decided tint, and is distinguished by its yellow colour. It is soft and very malleable, and can be beaten out into thin leaves (*gold-leaf*). It can be hammered so thin as to transmit light, the light being of a bluish-green colour. Gold is too soft a metal for general use, and is therefore alloyed with copper, in order to produce a hard alloy, which does not so readily wear away when used. The fineness of a sample of gold is in England expressed in *carats*, pure gold being said to be 24 carats. Thus, 18-carat gold consists of 18 parts of gold alloyed with 6 parts of copper; 15-carat gold consists of 15 parts of gold alloyed with 9 parts of baser metal, and so on. English sovereigns and half-sovereigns are made of 22-carat gold—that is, of 22 parts of gold alloyed with 2 parts of copper.

Gold is not attacked by sulphuric, hydrochloric, or nitric acids separately; it is acted on by aqua regia (nitro-hydrochloric acid), auric chloride (AuCl_3) being formed, and nitric oxide evolved.



“Fulminating gold” is an extremely explosive ammoniacal compound of gold.

PLATINUM

Symbol, Pt; tetrad; atomic weight, 195; specific gravity, 21.7; melts at 1710°.

Platinum occurs in nature in the metallic state mixed with quartz. It is a very tough metal, and on account of its high melting-point and indifference to acids, is very suitable for the manufacture of crucibles, dishes, etc., used for analytical work. Platinum may be obtained as a grey spongy mass, called *spongy platinum*, by heating the chloro-platinate of ammonium $(\text{NH}_4)_2\text{PtCl}_6$; this spongy platinum is very porous, and possesses the power of occluding, or condensing within its pores, oxygen from the atmosphere. The occluded oxygen is so active that, if a stream of hydrogen is directed on to spongy platinum, the platinum first becomes red-hot, and then ignites the hydrogen. Döbereiner's hydrogen lamp depends upon this property of spongy platinum igniting a jet of hydrogen.

Platinum is not attacked by sulphuric, hydrochloric, or nitric acids separately; it is acted on by aqua regia (nitro-hydrochloric acid), with formation of chloro-platinic acid, H_2PtCl_6 .

THE FOUR METALS COMPARED

Three of the metals discussed in this chapter—viz. copper, silver, and gold—find their place, in the periodic classification (page 88), in the first column, following under the metal sodium; their points of resemblance with that metal are not numerous,

whereas their points of difference are striking. Thus, they do not decompose water at ordinary temperatures; they occur in nature in the metallic state. Silver is a monovalent metal, and resembles sodium in the fact that it forms an alum with aluminium sulphate; on the other hand, copper is divalent and gold trivalent in their most characteristic compounds. Platinum comes in the eighth column, among the metals fusible with difficulty. By some chemists the metals mercury, silver, gold, and platinum have been classed together as the *noble* metals, because their oxides are reduced to the metallic state by the action of heat alone. Copper and gold are related in colour. The four metals, copper, silver, gold, and mercury, possess in common a singular property of forming curious ammoniacal compounds.

PART IV.—ORGANIC CHEMISTRY

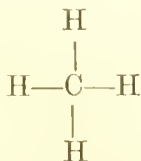
CHAPTER I

GENERAL PRINCIPLES

Organic Compounds—Organic Radicles—Destructive or Dry Distillation—Decay—Fermentation—Putrefaction.

ORGANIC chemistry includes the chemistry of the organic compounds. The term *organic* is derived from ὄργανον, *an organ*. Originally organic chemistry only included the chemistry of those compounds formed in plants and animals as the result of the vital processes occurring in their cells and tissues; at that time it was believed that these compounds could not be prepared artificially, but were only formed as the result of the vital processes taking place in plants and animals. This distinction was first proved to be erroneous by Wöhler, who, in 1828, artificially prepared *urea*, a well-known end-product of vital processes. Since that time many other organic compounds have been artificially prepared, often by direct syntheses from elements. We therefore know that the fundamental distinction which seemed to justify the separation of organic chemistry from inorganic does not really exist. The phenomena of both are controlled by the same laws. The division, no longer founded on principle, is maintained for convenience; certain special features do broadly distinguish the one from the other. To some of these we shall now refer.

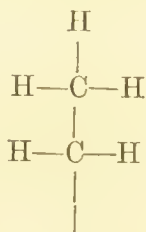
All organic bodies contain the element **carbon**. This element is a tetrad, and is represented as employing its full valency in the compound "marsh gas" (CH_4), to which the following graphic formula is assigned :—



Carbon has, moreover, a remarkable power of linking itself atom to atom, to form with other elements stable compounds of great complexity. To hæmoglobin, for instance, the red colouring matter of the blood, Preyer has assigned the formula $\text{C}_{600}\text{H}_{960}\text{N}_{154}\text{FeS}_3\text{O}_{179}$; while Linoffsky found $\text{C}_{712}\text{H}_{1130}\text{N}_{214}\text{FeS}_2\text{O}_{245}$. Both formulæ recognise the great complexity of the substance. No other element seems capable of forming compounds of such complexity. As carbon plays such an important part, organic chemistry has been sometimes defined as *the chemistry of the carbon compounds*, excluding the two oxides and the sulphide of carbon (CO , CO_2 , CS_2), which are usually classed as inorganic substances.

We may look at organic chemistry from another point of view, which is very instructive. In the inorganic part the number of elements is large, but the number of compounds of any one element is comparatively small. In the organic compounds the number of elements is small, but the number of the compounds of these few elements seems almost unlimited. The elements, in fact, of the inorganic portion are represented in organic bodies by the groups of elements called **radicles** (see page 26). The element potassium forms, as we have seen, an oxide, hydroxide, chloride, sulphate, etc.; parallel series of compounds are formed by many organic

radicles, as, for instance, by the radicle ethyl (C_2H_5) ; this is a monovalent radicle, with the graphic formula



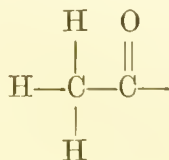
This radicle forms a hydroxide (ordinary alcohol), an oxide (ordinary ether), etc. So completely does it act the part of an element that it is often represented by a single symbol, Et ; the parallel series of ethyl compounds will therefore be—

K'	$(\text{C}_2\text{H}_5)'$	or	Et'
KOH	$(\text{C}_2\text{H}_5)\text{OH}$..	EtOH
K_2O	$(\text{C}_2\text{H}_5)_2\text{O}$..	Et_2O
KCl	$(\text{C}_2\text{H}_5)\text{Cl}$..	EtCl
K_2SO_4	$(\text{C}_2\text{H}_5)_2\text{SO}_4$..	Et_2SO_4
KNO_3	$(\text{C}_2\text{H}_5)\text{NO}_3$..	EtNO_3

There is a very large number of these radicles, and each forms its own compounds, just as each metal has its own oxides, salts, etc.

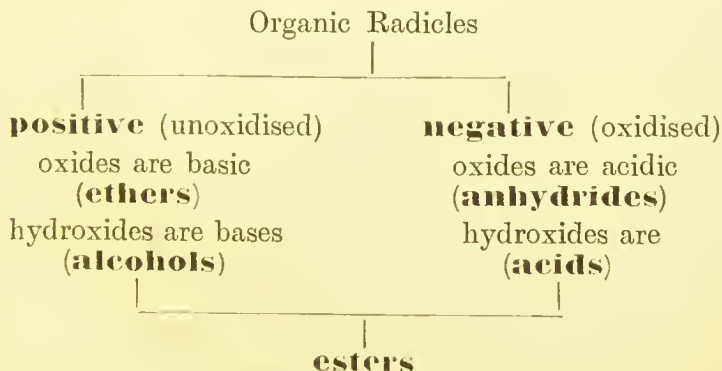
We have already distinguished two main types or classes of elements by the terms positive (metals) and negative (non-metals). We have also seen that this difference of type extends to the compounds of each, and gives rise to the two main classes of oxides and hydroxides of inorganic chemistry. It was mentioned, too (page 26), that two corresponding types of radicles also exist. The parallel between the elements and the radicles which now supply their place is indeed a much closer one than has yet been explained. The difference in type between the radicles is of precisely the same character as the difference between positive and negative elements, and is nearly always associated with the presence

or absence, in the radicle, of the negative element oxygen. Broadly speaking, then, we recognise two main types of radicles—*positive* (or unoxidised) radicles like ethyl, and *negative* (or oxidised) radicles like acetyl (CH_3CO)', whose graphic formula is



This also so closely imitates an element that it is often represented by a single symbol, Ac' .

The difference in type between the radicles extends, as with the elements, to their derivatives. We have again two classes of oxides, namely, ethers and anhydrides; two classes of hydroxides, namely alcohols and acids; finally, to complete the resemblance, we have ethereal salts (or esters) formed by the interaction of alcohols and acids, and therefore corresponding in origin and character with the inorganic *salts*. All these points of resemblance are presented in the following table, which should be carefully compared with the similar tabular statement on page 58:—



The cyanogen group $(\text{CN})'$ also functions as a

negative radicle, though unoxidised; but it forms no oxide, and it has other special features which indicate a closer relation to chlorine than to acetyl. Cyanogen and its compounds are indeed often considered with the inorganic substances.

Just as inorganic chemistry is the chemistry of the elements and their derivatives, so we might say that organic chemistry is the chemistry of these radicles and their derivatives.

It may be as well to caution the student against confusing organic bodies or compounds, such as these, with an *organised body*. An organised body is a tissue of fibrous or cellular nature, the result of animal or vegetable growth, and cannot be made artificially.

Elements composing organic compounds.

—Although the number of organic compounds far exceeds that of the inorganic bodies, yet the actual number of elements entering into the composition of the great majority of organic substances is small. One large group, the *hydrocarbons*, contains only two elements, carbon and hydrogen; another great class contains oxygen in addition: this includes the *carbohydrates* (starch, sugar, etc.) and most of the organic acids; in fact, a very large proportion of organic bodies are composed only of two or more of the four elements, carbon, hydrogen, oxygen, and nitrogen; chlorine, bromine, iodine, sulphur, and phosphorus enter into the composition of a few, whilst metallic elements are contained in a small number of organic bodies. The fact, however, should be borne in mind that any element can be made to enter into the composition of an artificially prepared organic compound.

Action of heat on organic bodies.—With the exception of those organic substances that volatilise unchanged when heated, most organic bodies

are distinguished by the facility with which they are decomposed on the application of heat. If heated to a sufficiently high temperature with free contact of air, they burn away, the carbon forming carbon dioxide, the hydrogen forming water, and the nitrogen escaping in the free state or as ammonia. If heated out of contact with the air, most organic bodies undergo a complex decomposition, known as *destructive* or *dry distillation*, a number of fresh bodies being produced by a rearrangement of the atoms of the organic molecule under the influence of dry heat, without contact of air. For examples of destructive or dry distillation, see pages 210, 498.

Decay.—Many moist organic substances when exposed to the air undergo a slow process of oxidation and so are gradually destroyed without sensible elevation of temperature; this slow combustion or oxidation is called *decay*.

Fermentation.—This name is applied to a class of decompositions that many organic bodies undergo in presence of a ferment. There are two classes of ferments, the *organised* and the *non-organised*. The *organised ferments* are microscopic organisms, as *yeast* or *torula cerevisiæ*, which produces alcoholic or vinous fermentation, *mycoderma aceti*, which produces acetous fermentation, and *penicillium glaucum*, which produces lactic and probably butyric fermentation.

The various micro-organisms (bacilli, etc.) that have been connected with several of the zymotic diseases, and appear to be the primary causative factors of the diseases, possibly act as ferments within the human body and produce organic poisons, the presence of which in the system may be the direct cause of the symptoms of the various diseases. The *non-organised* or *soluble ferments* (enzymes) act only in solution, and when isolated are obtained

as amorphous powders, as, for example, *pepsin*, the ferment contained in gastric juice, *ptyalin*, the ferment contained in saliva, and *trypsin*, a ferment contained in pancreatic juice.

In the case of the organised ferments, the fermentative process is probably due to the ferment growing and multiplying at the expense of part of the substance that is being acted on, the remaining part breaking up into simpler bodies, which are the products of fermentation; in other words, the ferment is regarded as feeding, for its growth and multiplication, on a small portion of the substance undergoing fermentation, and thus destroying the chemical balance of the remaining portion, so as to cause its resolution into simpler bodies.

Putrefaction.—This process is practically one of fermentation produced in nitrogenised organic bodies by bacteria and other ferments, and accompanied by the evolution of unpleasant-smelling gases, which are mainly compounds of sulphur and phosphorus, and in part, possibly, complex hydrocarbon gases and volatile nitrogenous bases. The conditions necessary for putrefaction are (*a*) the presence of a certain amount of air to start the process, (*b*) moisture, and (*c*) warmth. If air is excluded, as in the proper tinning of tinned provisions, and if bacteria and other ferments are previously destroyed by heat, then putrefaction does not occur. Disinfectants prevent putrefaction by their germicidal action; that is, by destroying the ferments that set up the putrefactive changes.

CHAPTER II

ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS

Determination of Carbon, Hydrogen, Oxygen, Nitrogen, Chlorine, Sulphur, Phosphorus, and Iron in Organic Bodies—Calculation of Formulæ from Percentage Composition—Empirical, Molecular, and Constitutional Formulæ—Isomerism.

SINCE so large a number of organic compounds only contain carbon, hydrogen, and oxygen, their ultimate analysis consists in determining the amount of carbon in the form of carbon dioxide, the amount of hydrogen in the form of water, the amount of oxygen being always determined by difference. The determinations of the amounts of other elements, such as nitrogen, chlorine, bromine, iodine, sulphur, and phosphorus, are always made separately.

Detection of carbon and hydrogen in an organic compound.—This is usually effected by heating the compound with copper oxide, as already described (*see* page 200), and identifying the carbon dioxide and water produced. The presence of carbon can in many cases be inferred from the fact that the compound chars when heated with strong sulphuric acid or alone.

Estimation of the carbon and hydrogen in an organic compound containing carbon, hydrogen, and oxygen.—A weighed quantity of the dried organic compound (sugar, for instance) is taken, and its carbon is converted into carbon dioxide, and its hydrogen into water, by

burning it in a stream of oxygen in a tube containing copper oxide; the water is collected in a previously-weighed calcium chloride tube (Fig. 38),

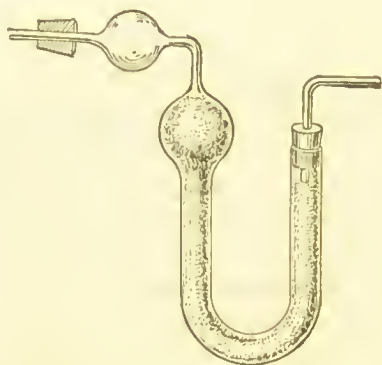


Fig. 38.—Chloride of calcium tube.

and the carbon dioxide in a strong solution of caustic potash contained in a series of bulbs (Fig. 39), which are weighed with the caustic potash previous to the operation.

The combustion is carried out in a thick com-

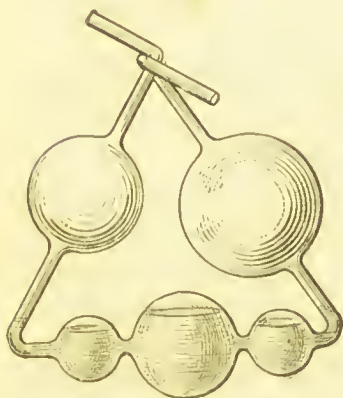
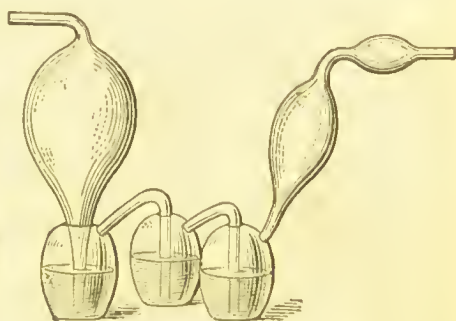


Fig. 39.—Liebig's potash bulbs.



Geissler and Mohr's potash bulbs.

bustion-tube, about 24 inches long, made of hard glass (Fig. 40), the fore part of which is charged with well-dried granular copper oxide c, a plug of

asbestos D being placed in front of it to prevent the mechanical carrying over of any of the copper oxide. The weighed quantity of sugar is placed in a small platinum boat B, which is then slipped into the tube as shown in the figure, and the tube is placed in a gas combustion-furnace, with the ends projecting from either extremity of the furnace; the weighed calcium chloride tube E is then connected to the end of the combustion-tube by means of a perforated cork, and the weighed potash bulbs (Fig. 39) are next connected to the calcium chloride tube at F by means of a small piece of india-rubber tubing; the hinder extremity of the tube at A is connected with a reservoir or gas-holder, from which pure dry oxygen can be passed through the apparatus.

The fore part of the tube containing the copper oxide is first made red-hot, and oxygen is allowed to pass slowly through the tube; heat is then applied to the part B where the platinum boat containing the sugar has been placed, when the sugar is burnt by the oxygen to carbon dioxide and water. Any hydrocarbon vapours that may escape combustion by the oxygen become completely oxidised during their transit over the red-hot copper oxide, some of which becomes reduced to cuprous oxide or to metallic

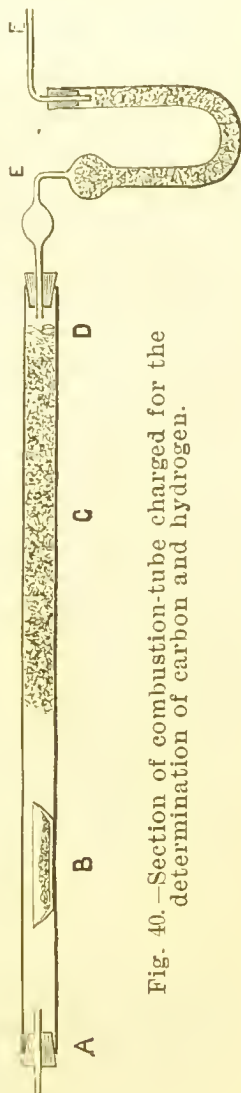


Fig. 40.—Section of combustion-tube charged for the determination of carbon and hydrogen.

copper. The water in the form of aqueous vapour (steam) and the carbon dioxide are carried onwards by the stream of oxygen, the water being entirely absorbed by the calcium chloride, and the carbon dioxide passing on is absorbed by the caustic potash in the potash bulbs. When all the sugar is completely burnt away, and nothing but oxygen bubbles through the potash bulbs, the operation is stopped, and the potash bulbs with the calcium chloride tube are detached and carefully weighed; the increase in weight of the latter gives the amount of water produced, and the increase in weight of the former gives the amount of carbon dioxide produced; from these the actual weights of carbon and hydrogen can easily be calculated. These, then, will be the weights of carbon and hydrogen that were present in the weighed quantity of sugar taken; from them the percentage composition of the sugar is finally calculated.

The following account of a combustion of sugar will illustrate the method of making these calculations:—

Weight of sugar employed	0.4	gram.
Weight of potash bulbs after the combustion	52.7425	„
Weight of potash bulbs before the combustion	52.1250	„
	<hr/>	
	.6175	gram. of CO ₂ produced.
Weight of calcium chloride tube after the combustion	33.4895	gram.
Weight of calcium chloride tube before the combustion	33.2575	„
	<hr/>	
	.2320	gram. of H ₂ O produced.

Now from the calculation of the molecular weight of CO_2 ,

$$\begin{array}{rcl} \text{C} & & = 12 \\ \text{O}_2 = 16 \times 2 & = & 32 \\ \hline & & 44 \end{array}$$

it is evident that every 44 parts of CO_2 contain 12 parts of C by weight; therefore what weight of C will be contained in .6175 grm. of CO_2 ?

$$44 : .6175 :: 12 : x$$

$x = .1684$ grm. of carbon, which is the weight of carbon present in .4 grm. of sugar.

Similarly, from the calculation of the molecular weight of H_2O ,

$$\begin{array}{rcl} \text{H}_2 & = 1 \times 2 & = 2 \\ \text{O} & & = 16 \\ \hline & & 18 \end{array}$$

it is evident that every 18 parts of H_2O contain 2 parts of H by weight; therefore what weight of H will be contained in .232 grm. of H_2O ?

$$18 : .232 :: 2 : x$$

$x = .0257$ grm. of hydrogen, which is the weight of hydrogen present in .4 grm. of sugar.

If .4 parts of sugar contain .1684 parts of carbon, what will 100 parts of sugar contain?

$$\begin{array}{l} .4 : 100 :: .1684 : x \\ x = 42.10 \text{ per cent. of carbon.} \end{array}$$

If .4 parts of sugar contain .0257 parts of hydrogen, what will 100 parts of sugar contain?

$$\begin{array}{l} .4 : 100 :: .0257 : x \\ x = 6.42 \text{ per cent. of hydrogen.} \end{array}$$

As sugar is composed only of carbon, hydrogen, and oxygen, if the sum of the percentages of carbon

and hydrogen be deducted from 100, the difference, viz. 51.48, will represent the percentage of oxygen.

	Percentage composition of sugar as obtained by analysis.		Percentage composition of sugar as obtained by calculation from its formula.
Carbon..	.. 42.10	..	42.11
Hydrogen	.. 6.42	..	6.43
Oxygen	.. 51.48	..	51.46
	<hr/> 100.00		<hr/> 100.00

Estimation of the carbon and hydrogen in an organic compound containing nitrogen.—The carbon and hydrogen are determined separately from the nitrogen. The process of combustion just described is adopted, but it is necessary to insert in the fore part of the tube at D (Fig. 40) a roll of copper gauze about 3 inches or 4 inches long. This is made red-hot before commencing the combustion, and reduces any oxides of nitrogen that may be evolved, converting them by abstraction of their oxygen into free nitrogen, which then passes unabsorbed through the calcium chloride tube and potash bulbs, and so escapes. If this were not done, any oxides of nitrogen formed would be absorbed by the caustic potash, and so would vitiate the determination of the carbon.

Estimation of the carbon and hydrogen in an organic compound containing chlorine, bromine, or iodine.—Lead chromate should be substituted for the copper oxide, and the combustion proceeded with in the usual manner, the lead chromate keeping back the halogen elements.

Estimation of the carbon and hydrogen in an organic liquid.—If it is required to determine the amounts of carbon and hydrogen in an organic liquid, such as alcokol, a bulb is blown

on the end of a piece of fine capillary glass tubing, the whole being of about the size shown in Fig. 41, so that it can be easily slipped into the combustion-tube. The bulb is first accurately weighed, it is then warmed over a spirit or Bunsen flame to expand the air within it, and its open end quickly inverted beneath some of the alcohol or whatever organic liquid is being submitted to analysis; as the air in the bulb cools and contracts, the alcohol is forced up into it by atmospheric pressure, and when the bulb is full of alcohol up to A, the end B is inserted for a moment or two into a spirit or Bunsen flame in order to seal it. The sealed bulb is now again weighed, and the increase of weight represents the amount of alcohol contained in it; the sealed end B is then broken off and is placed together with the bulb in the platinum boat (B, Fig. 40), which is then pushed into the combustion-tube, and the combustion proceeded with in the ordinary way, care being taken to apply heat very gradually to the part of the tube under the platinum boat, so that the alcohol shall be slowly converted into vapour, which, carried by the current of oxygen over the red-hot copper oxide, becomes completely oxidised to carbon dioxide and water.

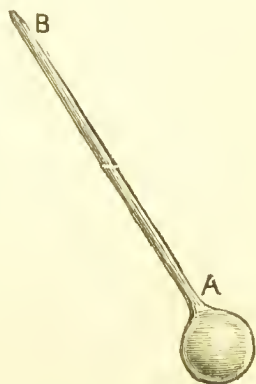


Fig. 41.—Bulb for weighing organic liquids.

Detection of nitrogen in an organic compound.—Many substances containing nitrogen, when heated on platinum foil, evolve the smell of burnt feathers; a better test is to heat the body with soda-lime, when most organic bodies containing nitrogen evolve ammonia, which can be recognised

by the ordinary tests ; the most satisfactory method is to heat a small quantity of the substance in a test-tube with a small piece of freshly-cut metallic sodium. When cold the mass is extracted with water, the solution filtered, boiled with a mixture of ferrous sulphate and ferric chloride, and finally rendered acid with hydrochloric acid ; if the original substance contained nitrogen, the acid fluid will be dark blue, or yield a blue precipitate. By the action of the sodium, sodium cyanide (NaCN) is formed ; this, by boiling in the alkaline solution, is converted by the iron salts into sodium ferrocyanide, which, when acidified, gives with the ferric salt Prussian blue.

An alternative—and perhaps more delicate—test is to evaporate a portion of the filtered extract (containing sodium cyanide) with a little ammonium sulphide to dryness *on the water bath* ; the dry residue will now contain sodium sulphocyanide, and will therefore show a blood-red colour after acidulation with dilute hydrochloric acid and addition of a few drops of ferric chloride.

Estimation of nitrogen in an organic compound.—The nitrogen of an organic compound is always determined separately from the carbon and hydrogen by a special process. There are three methods in use : 1, *The soda-lime process*, by which the nitrogen is converted into ammonia, the amount of which is estimated. 2, *The Kjeldahl process*, in which the substance is heated with strong sulphuric acid and the nitrogen converted into ammonium sulphate. 3. *Dumas' method*, by which the nitrogen is evolved in the free state and measured.

1. *The soda-lime process*, or *Will and Varrentrapp's method*.—This process depends upon the fact that if an organic nitrogenous body is heated with a solid caustic alkali, the nitrogen is converted into and is completely evolved as ammonia. A piece of

stout combustion-tubing, about 15 inches long, is drawn out to a point at one end, which is bent nearly to a right angle (Fig. 42); the posterior third of this



Fig. 42.—Combustion-tube for the determination of nitrogen by the soda-lime process.

(A, Fig. 43) is filled with the granular soda-lime (a mixture of sodium and calcium hydrates, produced by slaking lime with a strong solution of caustic soda); the weighed quantity of the nitrogenous organic substance is then thoroughly mixed with more soda-lime, and the mixture introduced into the combustion-tube so as to occupy the middle third (B, Fig. 43); the anterior third of the tube is filled up with soda-lime (C, Fig. 43), in front of which is placed a plug of asbestos D, to prevent the mechanical carrying over of any of the soda-lime. To the charged

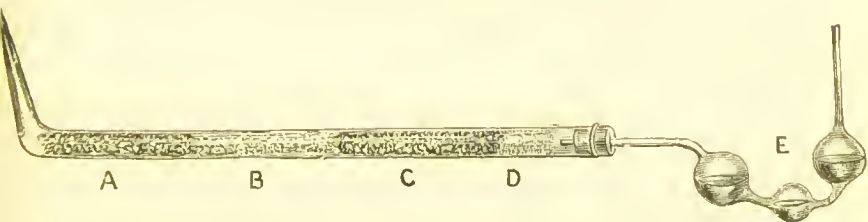


Fig. 43.—Combustion-tube charged for the determination of nitrogen by the soda-lime process.

combustion-tube is now fitted, by means of a perforated cork, the piece of apparatus, E (Fig. 43), consisting of three bulbs, and containing a measured quantity of dilute sulphuric acid of known strength. Heat is then applied to the fore part of the tube (C and D), and when this has become red-hot the

other portions of the tube are gradually heated, until the whole is red-hot. The nitrogen of the organic substance is converted by the soda-lime into ammonia, which as it bubbles through the diluted sulphuric acid contained in the bulbs is absorbed, neutralising some of the sulphuric acid. When no more bubbles pass through the acid the turned-up extremity of the combustion-tube is broken off, and air is drawn through the apparatus, so as to displace any ammonia remaining within the combustion-tube into the acid. The bulbs are then withdrawn and the acid turned out into a beaker; the amount of free acid left is determined by seeing what quantity of a standard solution of caustic soda is required to neutralise the acid left unneutralised by the ammonia; the difference between this amount and the amount originally required by the standardised sulphuric acid represents the amount of acid neutralised by the ammonia, from which the amount of ammonia required to neutralise it can easily be calculated. The weight of nitrogen contained in this amount of ammonia then represents the actual weight of nitrogen contained in the weighed quantity of the organic nitrogenous substance operated on, from which the percentage of nitrogen is easily calculated.

2. *The Kjeldahl process.*—In this process the nitrogen of the organic substance is converted into ammonium sulphate, while the carbon is oxidised. These changes have already been illustrated by the action of oil of vitriol on potassium ferrocyanide (page 201). From .2 to .8 gram. of the substance is placed in a round-bottomed flask with long neck, and from 10 c.c. to 20 c.c. of strong sulphuric acid are added. The flask is then heated, in a fume cupboard, over a low flame till the dark charred liquid is clear and colourless. The time taken to reach this stage varies much with different substances. Potas-

sium sulphate (about 10 grm.) is sometimes added. Copper sulphate, potassium permanganate, and other oxidising substances have also been employed in refractory cases. But strong sulphuric acid alone is often sufficient, though the addition of potassium sulphate can be safely recommended. The student must, however, remember that all materials employed must be free from ammonium salts, and this is an additional reason for introducing no unnecessary reagent. In many cases a "blank" experiment is conducted to test the purity of the materials in this respect. When the liquid has become clear and colourless it is—

- (1) Allowed to cool.
- (2) Poured, when cold, into cold distilled water, and the mixture made up to definite volume (say 200 c.c.).
- (3) Half this volume is reserved in case of accidents, and the other half is transferred to a distilling flask.
- (4) To this distilling flask a few drops of methyl orange are added, and then strong caustic soda solution, till the sulphuric acid is *nearly* neutralised.
- (5) The flask is now connected to a condenser, a few pieces of granulated zinc (pure, redistilled) are added to prevent bumping, and finally excess of caustic soda; it is then quickly corked and the contents distilled.
- (6) The ammoniacal distillate is received in 10 or 20 c.c. of decinormal sulphuric acid, containing two or three drops of methyl orange.
- (7) When all ammonia has come over, the distillate (which must still be red and

have remained red all the time, more decinormal acid being added if necessary from time to time) is titrated with decinormal soda.

Ex.—Suppose $\cdot 308$ gram. of substance were taken and 15 c.c. of $\frac{N}{10}$ H_2SO_4 were used to receive the distillate and 4 c.c. of $\frac{N}{10}$ $NaOH$ were used in titration (7);

Then the NH_3 evolved has neutralised $(15-4) = 11$ c.c. of $\frac{N}{10}$ H_2SO_4 , and must therefore be equal to 11 c.c. of $\frac{N}{10}$ NH_3 , that is, to $11 \times \cdot 0017$ gram. of NH_3 .

But this was obtained from one half of the sample, therefore $\cdot 308$ gram. evolve $22 \times \cdot 0017$ gram. of NH_3
 and contain $22 \times \cdot 0014$ gram. of nitrogen;
 therefore 1 gram. contains $\frac{22 \times \cdot 0014}{\cdot 308}$ gram. of nitrogen;
 therefore 100 gram. contain $\frac{22 \times \cdot 0014 \times 100}{\cdot 308}$ gram. of nitrogen,

\therefore the sample contains 10 per cent. of nitrogen.

3. *Dumas' method*.—This consists in burning the organic nitrogenous substance with copper oxide, passing the oxides of nitrogen formed over heated metallic copper, to reduce them to nitrogen, and collecting the nitrogen in a graduated tube over a strong solution of caustic potash, which absorbs carbon dioxide, but not nitrogen. Before commencing the combustion, the air within the charged combustion-tube is expelled by means of carbon dioxide. To carry out this process, a piece of combustion-tubing, about 25 inches long, is sealed at one end, test-tube fashion; at the closed end some

sodium bicarbonate A (Fig. 44) is introduced, then some copper oxide B, then the mixture of copper oxide and the weighed quantity of the organic nitrogenous substance C; after this some more copper oxide D, and finally a roll of metallic copper gauze E. A piece of bent tubing, dipping beneath the surface of mercury in a pneumatic trough, is then connected to the charged combustion-tube by means of a perforated cork. Before the graduated tube F is placed over the delivery tube, heat is applied to the sodium bicarbonate at A, so that the carbon dioxide evolved shall chase out all the air in the combustion and delivery tubes. When this is effected, the heat is removed from the end A, the graduated tube F is filled two-thirds with mercury and one-third with a strong solution of caustic potash, and inverted over the end of the delivery tube which is beneath the surface of the mercury in the trough. The combustion is carried on by first making the forepart of the combustion-tube at E red-hot, and gradually extending the heat to the hinder part till it is red-hot throughout. Any oxides of nitrogen formed are reduced by the

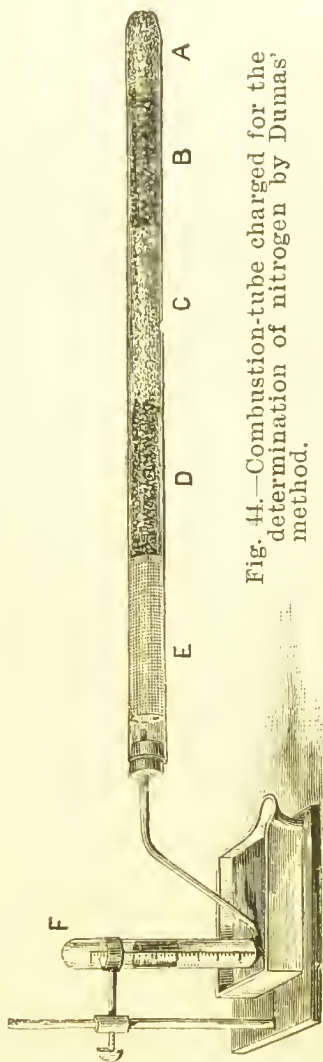


Fig. 44.—Combustion-tube charged for the determination of nitrogen by Dumas' method.

metallic copper to free nitrogen, which, along with carbon dioxide, bubbles up through the mercury and caustic potash in the graduated tube, the carbon dioxide being completely absorbed by the caustic potash and only the nitrogen collecting. When the nitrogen ceases to be evolved, the end A of the tube is again heated, so as to evolve carbon dioxide, which expels any nitrogen remaining in the combustion-tube. The volume of nitrogen is then read off, from which the weight can be calculated, and this represents the actual weight of nitrogen that was present in the weighed quantity of the organic nitrogenous body operated on.

Detection of chlorine in organic compounds.—When the compound is heated with sodium, as in the detection of nitrogen (page 406), any chlorine present will form sodium chloride. This will also dissolve when the fused mass is extracted with water, and the filtered solution, after proper treatment, can be tested for chloride by the usual tests.

Estimation of chlorine in organic compounds.—A weighed quantity of the organic compound is heated with pure quicklime (CaO) in a combustion-tube, by which means the chlorine of the organic compound is converted into calcium chloride; the contents of the tube are then dissolved in dilute nitric acid, and silver nitrate added to precipitate all the chlorine as silver chloride, which is collected, washed, dried, and weighed. From the weight of silver chloride the amount of chlorine present is calculated, and this will be the actual amount of chlorine present in the weighed quantity of the organic compound operated on.

Iodine and bromine in organic compounds are detected and estimated in a precisely similar manner.

Detection of sulphur in organic compounds.—When the substance is heated with sodium,

sulphur, if present, forms sodium sulphide, which can be identified as usual in the alkaline filtrate obtained as before after extracting the fused mass with water.

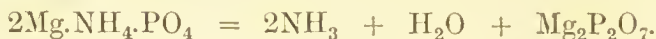
Estimation of sulphur in organic compounds.—A weighed quantity of the organic compound is heated in a sealed tube with fuming nitric acid for two hours, by which means the sulphur is oxidised to sulphuric acid; the contents of the tube are boiled with water, and filtered; to the filtrate barium nitrate is added to precipitate the sulphuric acid as barium sulphate, which is collected, washed, dried, and weighed. From the weight of barium sulphate the amount of sulphur present is calculated.

Detection of phosphorus in organic compounds.—The method just described for the estimation of sulphur may be used both for the detection and estimation of phosphorus. In the former case the quantity of the substance taken need not be weighed, and the phosphoric acid formed need not be estimated. It may be identified by the usual tests (page 228).

Phosphorus can also be detected by fusing the organic compound with fusion mixture and potassium nitrate. In this case the phosphorus will form an alkaline phosphate, soluble in water, and therefore easily identified in the aqueous extract after proper treatment.

Estimation of phosphorus in organic compounds.—As already stated, the phosphorus is estimated as phosphoric acid after oxidation by nitric acid as in the estimation of sulphur. The acid is precipitated as ammonium magnesium phosphate ($\text{Mg.NH}_4.\text{PO}_4$) by the addition of *magnesia mixture* (an ammoniacal solution of magnesium and ammonium chlorides). The crystalline precipitate when complete is collected on a filter, washed, dried, and

ignited. It is thus converted to magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), and is weighed in this form.



Detection of iron in organic compounds.

—When an organic compound containing iron is strongly heated, the organic matter is gradually burned away and the iron remains, either in the form of oxide or of the metal itself, having been reduced by the carbon of the organic substance. In either case, the residue will dissolve in hydrochloric acid and produce a solution of chloride of iron to which the usual tests (*see* page 375) can be applied.

Estimation of iron in organic compounds.

—The solution of chloride of iron, which has just been referred to, will probably contain the iron partly in a ferrous state and partly in a ferric. For purposes of estimation, it is more convenient (1) to convert it entirely into the ferrous state (page 374), and then estimate it volumetrically (page 599), or (2) to convert it entirely into the ferric state (*see* page 373), and then estimate it gravimetrically as ferric oxide (Fe_2O_3), obtained by igniting the precipitate produced by the addition of excess of ammonia solution to the ferric chloride solution.

CALCULATION OF THE FORMULA OF A COMPOUND FROM THE PERCENTAGE COMPOSITION

The student has already learned that our formulæ do not represent the composition of 100 parts by weight of each of the various substances. He knows that they represent the composition of the different molecular weights of the different substances. It is therefore not the percentage composition, but

the composition of the molecular weight that we wish to know. *If we know the molecular weight* it is more useful to state our results in that form than as a percentage. The percentage composition is, in fact, mainly useful as a step to this molecular composition. Our formulæ differ in another respect from the percentage statement. They represent the composition, not in unit parts by weight, but in *atoms*. The formula As_2O_3 , for instance, does not represent 2 parts by weight of arsenic and 3 parts by weight of oxygen, but 2 *atoms* of arsenic and 3 *atoms* of oxygen ; this is really equivalent to 150 parts by weight of arsenic and 48 of oxygen.

In order that our percentage statement should represent the result in *atoms*, it is clear that we must divide each percentage weight by the atomic weight of the element to which it refers. For instance, the percentage composition of acetic acid, as determined by ultimate analysis, is—

Carbon	40.00
Hydrogen	6.66
Oxygen	53.34
		<hr/>
		100.00

Dividing each percentage weight by the respective atomic weight we obtain—

Carbon	40.00	÷	12	=	3.33	atoms.
Hydrogen	6.66	÷	1	=	6.66	„
Oxygen	53.34	÷	16	=	3.33	„

The quotients so obtained represent the percentage composition in *atoms*. Of course, we cannot really have a *fraction* of an atom, and there would be no fraction in these quotients if we stated the composition of the molecular weight, because the molecule only contains integral atoms. The percentage

molecule is an imaginary one. Realising, therefore, that these quotients must be converted into whole numbers, while preserving, of course, their relative proportions, we now divide them all by the lowest, thus :

Carbon	3.33	÷	3.33	=	1 atom.
Hydrogen	6.66	÷	3.33	=	2 atoms.
Oxygen	3.33	÷	3.33	=	1 atom.

and arrive at the formula CH_2O .

This is the *empirical formula* of acetic acid ; that is, it is the simplest possible expression of its composition, representing the elements of which it is composed, and their relative proportions in *atoms*. A *molecular formula* indicates the number of atoms in the molecule of a body, and may be the same as the empirical formula, or some simple multiple of it. To ascertain the molecular formula of acetic acid, its vapour-density may be taken ; that is, it may be converted into vapour, and the specific gravity of its vapour determined. The molecular weight is obtained by doubling the vapour-density, since the specific gravity of any gas or vapour is half its molecular weight (see page 31) ; it can then be easily ascertained whether this molecular weight is the same as that calculated from the empirical formula, or is some multiple of it.

Now, the vapour-density of acetic acid is 30 (that is, its vapour is 30 times heavier than hydrogen at the same temperature and pressure), therefore the molecular weight of acetic acid is 60. The formula CH_2O only gives a weight of 30.

$$\begin{array}{rcl}
 \text{C} & & = 12 \\
 \text{H}_2 = 1 \times 2 & = & 2 \\
 \text{O} & & = 16 \\
 & & \hline
 & & 30
 \end{array}$$

Therefore, the double of the empirical formula, viz. $C_2H_4O_2$, must be the molecular formula of acetic acid, since it yields the molecular weight of acetic acid, viz. 60.

$$\begin{array}{rcl}
 C_2 & = & 12 \times 2 = 24 \\
 H_4 & = & 1 \times 4 = 4 \\
 O_2 & = & 16 \times 2 = 32 \\
 \hline
 & & 60
 \end{array}$$

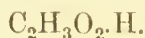
A *constitutional* or *rational formula* indicates not only the number of atoms in the molecule of a body, but also the way in which those atoms are arranged; that is, it exhibits the constitution or architecture of the body.

This architecture is in some way very closely associated with the properties of the body. A change in the arrangement of the *same* atoms is accompanied by a change in properties. The group — C — H

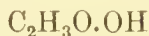


confers properties quite distinct from those conferred by the group —C—O—H. The student will soon meet with many similar illustrations, and will find abundant evidence that, in organic chemistry, interest and importance are attached rather to *groups* than to individual elements. Reactions, therefore, which enable us to detect the presence of any particular group in a substance become of first-rate importance. One such reaction has been mentioned in connection with the pentachloride of phosphorus (page 235). There are, of course, many organic compounds of which we do not yet know the constitutional formulæ. Acetic acid, however, is not one of them. In this case we know that when one of the four hydrogen atoms is replaced by sodium, or some other metal, the substance is no longer an acid, though still containing three hydrogen atoms. We therefore recog-

nise the special character of this hydrogen atom and write the formula :—



We also find that this is the hydrogen atom that disappears in company with an oxygen atom when phosphorus pentachloride acts upon acetic acid and replaces hydroxyl (OH) by chlorine, forming acetyl chloride (page 235) ; we may now write our formula—



We know, too, that when sodium acetate is heated with sodium hydroxide, marsh gas and sodium carbonate are formed, thus :



When we remember that the *constitutional* formula of sodium carbonate is $\begin{array}{c} \text{ONa} \\ \text{C}=\text{O} \\ \text{ONa} \end{array}$ (page 62),

we see that the C = O group must be present in sodium acetate and therefore in acetic acid. These compounds must also contain a CH₃ group to account for the formation of marsh gas (CH₄). We have now dissected the molecule of acetic acid into its constituent groups, and can write the formula—



The group CO.OH or, graphically, $\begin{array}{c} \text{—C—O}\cdot\text{H} \\ \parallel \\ \text{O} \end{array}$

called carboxyl, and is present, not only in acetic acid, but in every member of a very large class of organic acids which are therefore called carboxylic acids. It is an important illustration of the *class-group*, which plays so prominent a part in organic chemistry. Every important class of organic compounds has its characteristic class group, to which

the leading features common to each member of the class are due.

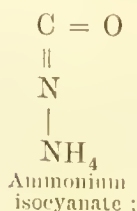
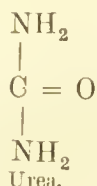
ISOMERISM

Since the empirical formula is deduced, as we have shown, from the percentage composition, it follows that all substances which have the same percentage composition must also have the same *empirical* formula. They may, or may not, have the same *molecular* formula, which, as we have seen, is either the same as the empirical formula, or is some multiple of it. To determine this multiple requires a knowledge of the molecular weight of the substance *in addition to* the percentage composition. Substances which have both the same empirical formula and the same molecular formula are generally described as *isomeric* substances (from ἴσος, *equal* ; μέρος, *part*). and one is called an *isomer* of the other. When the empirical formulæ are the same but the molecular formulæ different, one being a multiple of the other, we have what is called *polymerism* (from πολλός, *many* ; μέρος, *part*) and the substance of higher molecular weight is called a *polymer* of the other.

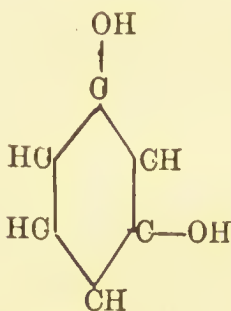
Ex.—Benzene (C_6H_6) is a polymer of acetylene (C_2H_2).

Isomeric bodies, as thus defined, have not the same *constitutional* formula, because, although the atoms that compose their molecules are the same in *nature* and in *number*, they are arranged in *different groups*. This confers upon them different properties, as we have seen, and makes them quite different individuals. Isomerism may, however, extend further: sometimes the atoms are even arranged in the same groups and the individuals are only distinguished by the fact that the groups themselves are differently placed. In urea, $CO(NH_2)_2$, and ammonium isocyanate,

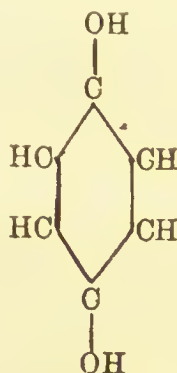
NH_4NCO , for instance, the atoms are arranged in different groups—



but in resorcin and hydroquinone the atoms fall into the same groups, but the groups have not the same situation in the molecule. Both are represented by the formula $\text{C}_6\text{H}_4(\text{OH})_2$, and the difference only appears in the *graphical* formulæ—



Resorcin.



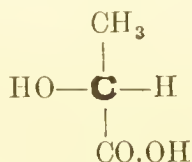
Hydroquinone.

This kind of isomerism is sometimes conveniently distinguished by the term *metamerism* (μετά, prefix implying *change, alteration*).

In certain special cases isomeric resemblance of a still closer character exists without quite becoming identity. The two molecules differ as a right-hand glove differs from the left-hand fellow to it. Although composed of identical constituent parts, the two complete structures really occupy different positions in space. This is proved by the fact that they cannot be made exactly to coincide. If, for instance, we

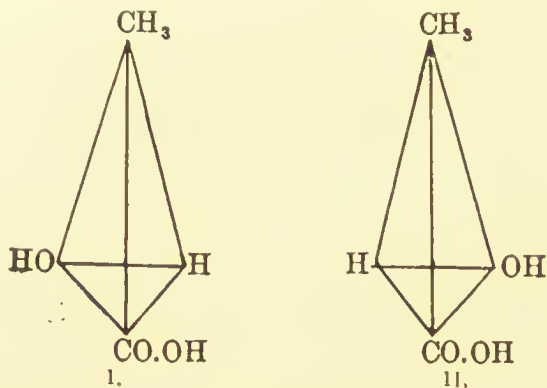
insert the left-hand glove into the other, so that the palms and backs of the pair shall coincide, then the thumbs and little fingers will *not*. If, on the other hand, we push thumb into thumb and little finger into little finger, etc., then the palms and backs will not coincide. If the thumb and little finger were alike, or the palm and back, coincidence would be easily secured. The difficulty is really due to the want of symmetry in the hand—the fact that *all its four aspects are different*.

Now, a saturated carbon compound in which the four valencies of a carbon atom are combined with four *different* elements or groups will also possess this special feature. Such a carbon atom is in fact described as *asymmetric*. One is present in the molecule of lactic acid, and is printed in thick type in the graphical formula below :—



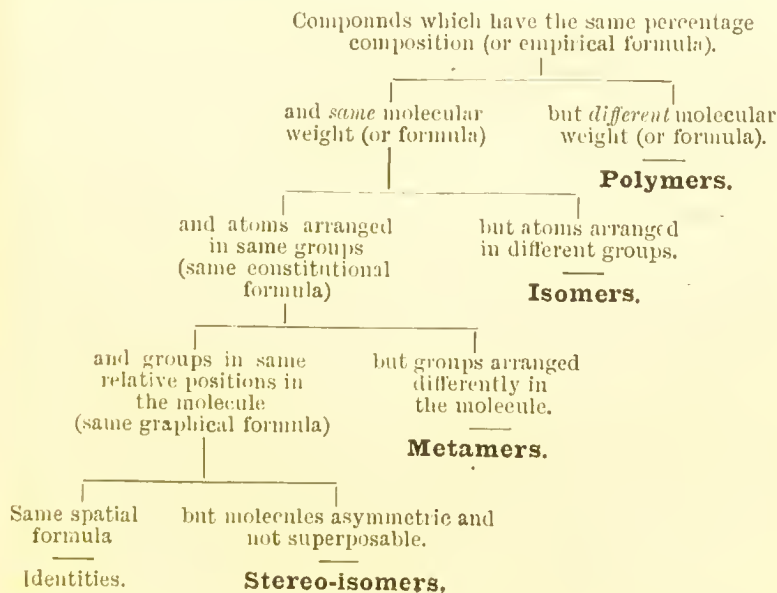
The right-hand or *dextro* molecule, and the left-hand or *levo* molecule, are both known. A mixture of equal numbers of both molecules constitutes the ordinary fermentation lactic acid of sour milk. To illustrate the difference between the two molecules we shall find it convenient to use a *solid* figure instead of a plane one. Imagine, for instance, that the asymmetric carbon atom (not shown in the diagrams on page 422) is placed at the centre of gravity of the tetrahedron, and that the four different groups with which it is associated are placed at the four angular points. It will be found that two arrangements are possible, such that one tetrahedron, even if hollow, cannot be slipped over the other, so as to make all

four similar groups coincide at the same time. Only these two arrangements are possible, and it will be seen that II. is the image of I. as seen in a plane mirror.



In these cases the atoms are not arranged in different groups, as in the isomers, urea, and ammonium cyanate, already referred to; nor is the *relative* arrangement of the groups in the molecule altered, as in the metamers resorcin and hydroquinone, figured on page 420; the difference is due to alteration in the spatial arrangement of the molecule *as a whole*, regarded as a solid figure. We might therefore say that in these cases empirical, molecular, and constitutional formulæ are the same, but spatial formulæ are different, and show a want of coincidence. This phenomenon has been described as *stereo-isomerism*, which means, literally, *solid-figure isomerism* (Gk. στερεός, *solid*). It is also sometimes called *physical isomerism*, because two molecules so related usually differ in physical, rather than chemical, properties. Curiously enough, one of their best-known differences is of a right-handed and left-handed character; one molecule rotates the plane of polarised light to the right hand, while its counterpart rotates it to the left. Even in their crystalline form, the visible crystals reflect the same

peculiar distinction which is believed to exist in the invisible molecules; this was well shown in the case of the dextro and lævo modifications of tartaric acid by the famous experiment of Pasteur. It may be worth while, in conclusion, to warn the student that the terms employed in this section are not always quite so rigidly or precisely applied as we have seemed to suggest. The subtler shades of resemblance were not known when the terms isomerism and metamerism were first adopted. Hence they have acquired a somewhat vaguer and more extended meaning as time went on and knowledge widened; and the student will sometimes find the terms isomer and metamer used almost as synonyms. He is recommended, however, while the subject is new to him, to use different names for different things, and, as far as possible, to avoid using more than one name for the same thing. The classification discussed in this section will perhaps be more clearly seen in the following tabular scheme:—



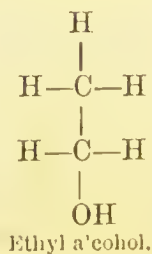
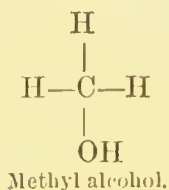
CHAPTER III

CLASSIFICATION OF ORGANIC COMPOUNDS

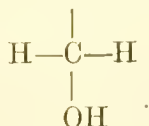
Chief Types — Alcohols — Aldehydes — Acids — Amines —
Amides — Nitriles — Carbamines — Nitro Compounds.

THE chief types of organic compounds are so closely related that a detailed discussion of one is almost impossible without reference to others. The student should therefore become acquainted with the name and general structure of each before proceeding to a fuller study of any particular type. Some have already been mentioned and their structure explained (page 395), e.g. *ethers*, *alcohols*, *acids*, *esters*, and *hydrocarbons*. They will be more fully discussed in subsequent chapters. From some of these, however, other types are derived which deserve mention. From hydrocarbons *halogen derivatives* are obtained by replacing hydrogen by chlorine, bromine, or iodine; thus from methane (CH_4) are derived chloroform (CHCl_3) and iodoform (CHI_3).

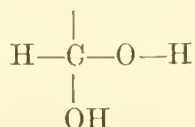
Aldehydes are derived from alcohols by oxidation. We have already seen that alcohols are the hydroxides of the hydrocarbon radicles, and that methyl and ethyl alcohol have the graphical formulæ—



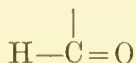
The molecules of these, and all similar alcohols, contain the same group, CH_2OH , or graphically



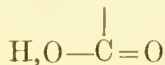
and this is one of the important *class-groups* to which reference has already been made (page 418). When one of these alcohols is oxidised we suppose that the active atom of oxygen at first attaches itself to the molecule between the C and H, producing the group



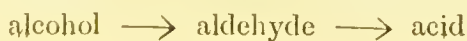
and this by loss of H_2O from the two OH groups (page 61) becomes



The body is now an aldehyde, and this is the group that characterises the class. Reducing power is one of the properties conferred by this group. It must therefore be easily oxidised. It is thus converted into the group



This is the carboxyl group already referred to (page 418) as being characteristic of a large class of organic acids. Aldehydes therefore act as good reducing agents, and themselves become oxidised to acids. For instance, they reduce an ammoniacal solution of silver nitrate to metallic silver (often obtained as a bright mirror on the test tube). The change



is thus attended by a change in the class group—



These changes do not affect the radicle to which the class-group is attached. This radicle is different for each member of the class, but the difference is a constant one (CH_2). Thus the radicle in the methyl series is H, and in the ethyl series CH_3 ; we have therefore—

$\text{H.CH}_2\text{OH}$
Methyl alcohol.

H.CHO
Formaldehyde
(Formic aldehyde).

H.CO.OH
Formic acid.

$\text{CH}_3.\text{CH}_2\text{OH}$
Ethyl alcohol.

$\text{CH}_3.\text{CHO}$
Acetaldehyde
(Acetic aldehyde).

$\text{CH}_3.\text{CO.OH}$
Acetic acid.

In the next series, the *propyl* series, the radicle is increased by another CH_2 and becomes C_2H_5 , but the class-groups of course remain unaltered. A succession of similar compounds, containing the same class-group attached to radicles which differ by this constant difference (CH_2), constitutes an *homologous series*. We have here the first two members of each of three homologous series—alcohols, aldehydes, acids.

Although the radicle is unaffected by changes in the class-group, it may undergo other alterations. The hydrogen in CH_3 may be replaced by chlorine, as in the case of methane (CH_4), and give rise to halogen derivatives of these ethyl compounds. Chloral or trichlor aldehyde is an instance, and has the formula $\text{CCl}_3.\text{CHO}$.

The classes hitherto discussed have not included compounds which contain nitrogen. To the classification of these we now proceed. It will be convenient to begin by dividing them into three main groups :

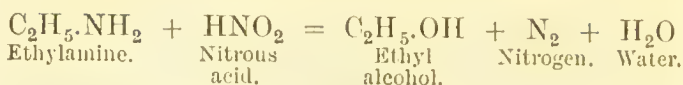
1. Derivatives of ammonia (NH_3).
2. Derivatives of cyanogen (CN).
3. Compounds containing oxidised nitrogen.

1. Many nitrogenous organic compounds may be regarded as derived from ammonia (NH_3) by replacing a hydrogen atom by a compound radicle. If this radicle is a positive one, the resulting derivative is called an **amine**; if the radicle is a negative one the derivative is an **amide**. Thus $\text{NH}_2(\text{CH}_3)$ or $\text{NH}_2\text{Me}'$ is *methylamine*, and $\text{NH}_2(\text{CH}_3.\text{CO})$ or $\text{NH}_2\text{Ac}'$ is *acetamide*. The amines are further subdivided into primary, secondary, and tertiary amines, according as one, two, or three of the hydrogen atoms in the NH_3 molecule are thus replaced. We shall seldom have occasion to refer to any but the primary amines. It will be seen that their *class-group* is NH_2 , and that they form another homologous series in which the radicle attached to the class-group differs in successive members by the usual increment CH_2 . We might, in fact, regard ammonia as the amine of hydrogen and the starting-point of the series, thus:

H.NH_2	Hydrogen amine (ammonia).
$\text{CH}_3.\text{NH}_2$	Methylamine.
$\text{C}_2\text{H}_5.\text{NH}_2$	Ethylamine

and so on. The student will notice that they only differ from the *hydroxides* of the corresponding radicles in having the group* NH_2 in place of the group OH . But these hydroxides are *alcohols*, and we find in fact that primary amines are readily converted into corresponding alcohols. Nitrous acid effects the conversion, which, is thus represented in the case of ethylamine:

* This group is called "Amidogen."



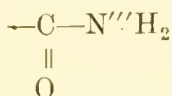
If we compare this reaction with the preparation of nitrogen from ammonium nitrite, which might be represented thus—



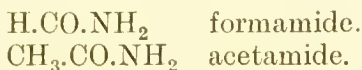
we see that the only real difference between the two equations is that the group C_2H_5 in the first is replaced by a single H in the second. The reactions are therefore essentially the same, and illustrate the close kinship both of the amines to ammonia and of the alcohols to water. As is only to be expected, the amines resemble ammonia in all essential chemical features—they function as bases of the ammonia type (page 163), forming salts by *addition* of the acid molecule by employment of valencies previously latent. Thus the chloride (or *hydrochlorate*) of ethyl amine is $\text{C}_2\text{H}_5.\text{N}^+\text{H}_2.\text{HCl}$. In physical characters also there is a similar close resemblance. The vapour and solution of ethylamine have a pungent ammoniacal odour, turn red litmus paper blue, and might, in fact, be easily mistaken for that of ammonia.

The amides, however, show a much less striking resemblance to ammonia, because the hydrogen has been replaced by a dissimilar *negative* radicle instead of by a very similar hydrocarbon radicle. The lower amines are vapours, like ammonia, or very volatile liquids, but acetamide is a colourless, crystalline, deliquescent solid which melts at about 80° and boils at 222° . Neither the solid nor its aqueous solution has an ammoniacal odour or an alkaline reaction. This amide is often found to have a strong odour of mice, which is believed to be due to the presence of an impurity. Acetamide and its homo-

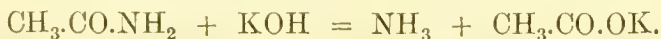
logues show only a comparatively feeble power of forming salts by addition like ammonia and the amines, but owing to the presence of the negative radicle an atom of the amidogen hydrogen is sometimes capable of being replaced by a metal. In these amides the NH_2 group is attached to the oxidised carbon atom, and they therefore contain the class-group CO.NH_2 , or, graphically—



They form an homologous series of which the first two members are



If the NH_2 were replaced by OH these would be the formulæ of formic and acetic acids. The amides therefore stand in the same relation to the carboxylic acids as the primary amines do to the alcohols. The conversion can be effected by nitrous acid in this case also. The connection to acetic acid is evident, too, in the behaviour of acetamide when warmed with solution of caustic potash; ammonia is evolved and the potassium salt of acetic acid is produced.

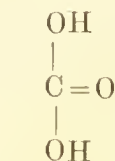


Ammonium acetate behaves in the same way, but in this case a molecule of water is separated also.

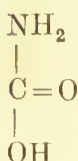


Acetamide is, in fact, prepared from ammonium acetate by removal of this molecule of water from the salt by distillation. By dehydration of other ammonium salts the corresponding amides can be obtained.

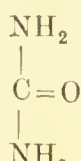
Dibasic acids contain *two* OH groups; when both are replaced by NH_2 the product is called an amide, but when only one is so replaced the product is called an *amic acid*, thus—



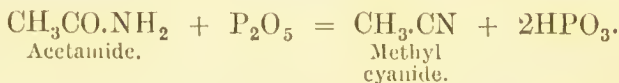
Carbonic acid.



Carbamic acid.

Carbamide
(urea).

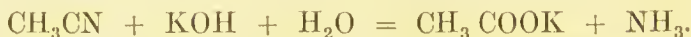
2. If the solid acetamide (or even ammonium acetate) be mixed with phosphorus pentoxide and distilled, dehydration proceeds further; the amide loses a molecule of water and a volatile liquid collects in the receiver. This liquid is **methyl cyanide**; it is formed from the amide thus:



It is one of a very important homologous series of compounds. These cyanides are readily converted by various reagents to other compounds, and therefore serve as convenient links leading from one class to another. Dilute acids, for instance, convert them into carboxylic acids, thus:

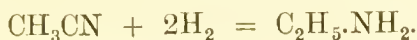


Aqueous alkalis act similarly, but in this case the alkali salt of the acid is formed:

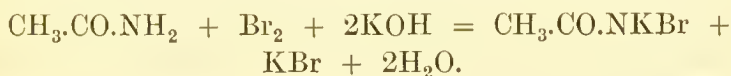


It is probable, therefore, that the conversion is really effected by the water, and that the acid or alkali merely accelerates it. Such a reaction is described

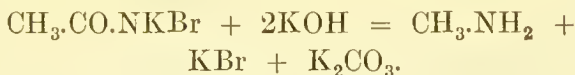
as **hydrolysis**, and the compound is said to have been hydrolysed. Nascent hydrogen reduces the cyanides to amines; thus methyl cyanide becomes ethylamine—



We can therefore pass from acetamide by means of the cyanide, to ethylamine. But *methylamine* can also be obtained from acetamide, and as this illustrates another general method for preparing a primary amine, we shall state it. Bromine is added to the amide, and then enough of a cold aqueous solution of caustic potash (about 10 per cent.) to make a pale yellow solution. The substances react thus:



On adding as much more caustic potash, and distilling, the reaction is completed, thus:



We know that the amines are converted into alcohols by nitrous acid, so that we can now pass from acetamide to methyl *or* ethyl alcohol.

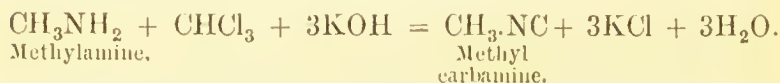
There is an isomer of methyl cyanide in which the methyl group is attached to the N of the CN group instead of to the C. It has therefore the formula $\text{CH}_3\cdot\text{NC}$, and is called methyl isocyanide; it is also known as methyl carbamine, because its formula resembles that of methylamine with C instead of H_2 . The cyanides are often known as the *nitriles* of the carboxylic acids on account of their ready conversion into these compounds. Thus

methyl cyanide which, as has been shown, so readily hydrolyses to acetic acid, is known as *aceto-nitrile*. This reaction also shows that in the nitrile the CH_3 group is attached to C, for we find it so in the acetic acid produced ($\text{CH}_3\text{CO.OH}$). On the other hand, when the carbamine is similarly hydrolysed, the reaction results thus—



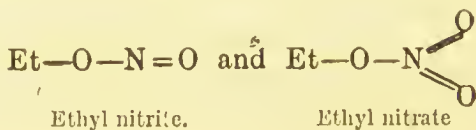
and we find the CH_3 group attached to N in the hydrochlorate of methylamine. We seem, therefore, justified in concluding that this is the connection existing in the carbamine.

Not only can the carbamines in this way be converted into primary amines, but the change may be reversed by warming an alcoholic solution of a primary amine, containing a little chloroform, with caustic potash, thus:

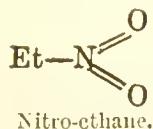


As a carbamine is easily recognised by its characteristic and unpleasant odour, this reaction is often employed as a test for a primary amine. Other, less important, cyanogen compounds will be referred to later, but need not be considered at present.

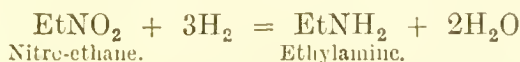
3. As already explained (page 394), the methyl and ethyl radicles and their homologues form compounds corresponding to those of potassium. Ethyl nitrite and ethyl nitrate contain *oxidised nitrogen*, their constitutional formulæ being (page 63)—



There is, however, an isomer of the nitrite which has the same *molecular* formula, EtNO_2 , but a different *constitutional* formula, thus :



In these *nitro* compounds the radicle is believed to be attached to the nitrogen atom, because they are readily reduced, by nascent hydrogen, to the amines, and in these compounds the radicle is known to be so attached :



Ethyl nitrite, however, is reduced to alcohol and ammonia ; and in alcohol we have seen that the radicle is attached to *oxygen*—



The nitro compounds are not true derivatives of nitrous acid at all ; they are more conveniently regarded as derived from nitric acid, and the most typical and stable examples—e.g. nitro-benzene (page 541)—are actually prepared by means of nitric acid. They are not, however, salts of this acid. In the formation of a nitrate it is only the hydrogen of nitric acid that is replaced by a radicle, but in the formation of a nitro compound the whole OH group of the acid is replaced by the radicle.

The student will now have become acquainted with the general nature of the chief types of organic compounds to which it will be necessary to refer. We shall therefore proceed to consider more fully some of the important classes to which his attention has been directed, and shall commence with the hydrocarbons.

CHAPTER IV

HYDROCARBONS

Paraffin Series: Methane—Ethane—Propane—Butane—
Pentane. Unsaturated Hydrocarbons: Ethylene—
Acetylene.

HYDROCARBONS are conveniently divided into—

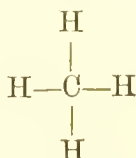
1. Saturated hydrocarbons (paraffins).
2. Unsaturated hydrocarbons.

PARAFFIN SERIES

The saturated hydrocarbons are really the *hydrides* of the radicles methyl, ethyl, and their homologues.* It has already been seen that these radicles are monovalent, as they have only one valency of one carbon atom unemployed. When this one is employed by attachment of a new hydrogen atom, every valency will be in use, and the compound formed will therefore be a *saturated* one. This saturated condition increases the stability of the hydrocarbon, and makes it appear deficient in chemical affinity; hence its name *paraffin* (from *parum affinis*, little affinity). They are not affected either by acids or by alkalis, but when mixed with chlorine and exposed to light, new compounds are formed by substitution of chlorine for hydrogen (page 438). The paraffins belong to an homologous series, of which the general formula is C_nH_{2n+2} ; therefore, by doubling the number of the carbon atoms, and adding two, the number of the hydrogen

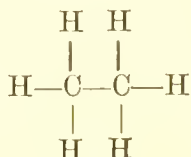
* They are sometimes called the *alkyl* radicles.

atoms in any particular paraffin will always be obtained. The first member of the series is methane or marsh gas (CH_4).



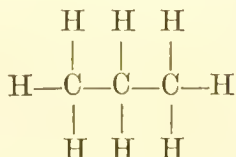
Graphic formula of methane.

The second or two-carbon *paraffin* is ethane (C_2H_6).



Graphic formula of ethane.

The three-carbon *paraffin* is propane (C_3H_8).



Graphic formula of propane.

The first four are gases, the next twelve are liquids, the rest are solids. Their occurrence in nature is not without interest.

In 1847 a small petroleum spring in a Derbyshire coal mine was discovered by the late Lord Playfair; this was purified and used for illuminating purposes. It soon, however, became exhausted, and in 1850 Young obtained a similar oil by distilling a hard, slaty coal. This industry still continues in Scotland. Soon after (in 1859) a bore-hole was made in search of petroleum at Titusville, in America, and a spring was struck yielding 800 gallons a day. Since

that date numerous springs have been discovered in America, Russia, and elsewhere.

Crude petroleum—or, as it is called in this country, paraffin oil—is a mixture of many paraffins and a small quantity of olefines. The latter are destroyed by agitation with strong sulphuric acid, the acid neutralised by soda, and the oil distilled in fractions, which are separated according to their boiling points. Thus, the most volatile portion, boiling at 40° — 70° , is known as petroleum ether; that boiling at 70° — 90° as gasolene; light petroleum, or benzoline, comes over at 80° — 120° . Then we have the portion boiling at 120° — 170° , which is sometimes used as a substitute for turpentine; next come the ordinary burning oils, known as “paraffin” or kerosene, boiling at 150° — 300° . Above these we have lubricating oils, vaseline, and various tarry substances; and, in the distillate from shale, paraffin wax.

Some lower members of the series will now be considered in detail.

METHANE (CH_4)

Known also as methyl hydride, *marsh gas*, *fire-damp*, and *light carburetted hydrogen*.

Modes of preparation.—1. By heating a mixture of sodium acetate and caustic soda, the latter being most conveniently employed in the form of soda-lime.



2. By passing a mixture of sulphuretted hydrogen and the vapour of carbon disulphide over red-hot copper.



3. Methane is produced by the slow decomposition of vegetable substances, as in marshes and stagnant pools, when it is known as *marsh gas*; it is also found in coal mines, where it is known as *fire-damp*. It issues from the earth in enormous volumes in certain localities, the Crimea, Pittsburg, and Heathfield in Sussex.

4. Methane is formed by the dry or destructive distillation of various organic substances, and is one of the chief constituents of coal gas (about 34 per cent.).

5. Marsh gas can also be produced by the action of water upon aluminium carbide (Al_4C_3).

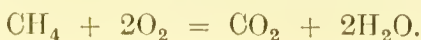
6. By the action of nascent hydrogen on methyl iodide.

7. By the action of water upon zinc methide, $\text{Zn}(\text{CH}_3)_2$

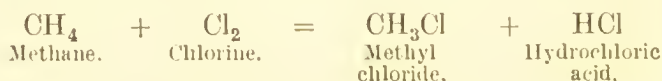


Properties.—A colourless, inodorous, and tasteless gas, condensing to a liquid at -164° , and having a critical temperature -99.5° .

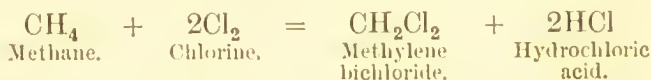
Its specific gravity ($\text{H} = 1$) is 8, and it is therefore much lighter than air; it is but very slightly soluble in water, and is combustible, but not a supporter of combustion. It burns with a feebly luminous flame, producing carbon dioxide and water. If mixed with oxygen or air, and a light applied to the mixture, an explosion will take place; this is the chief cause of the disastrous explosions that occur in coal mines. For complete combustion, methane requires *twice* its volume of oxygen and therefore *ten* times its volume of air. This is therefore the proportion which makes the most explosive mixture. The reaction is represented thus:



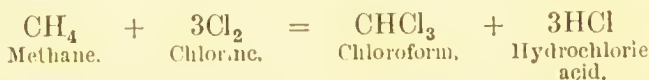
Methane is not poisonous, but it is incapable of supporting life. A mixture of methane and excess of chlorine, exposed to bright sunshine, explodes, forming hydrochloric acid and setting free carbon; but in diffused daylight chlorine acts upon methane slowly and quietly, forming a series of substitution products according to the amount of chlorine used. Thus, if equal volumes of methane and chlorine are employed, methyl chloride or monochlormethane (CH_3Cl) is formed.



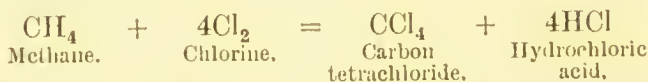
If 1 volume of methane and 2 volumes of chlorine are employed, bichloride of methylene or dichlormethane (CH_2Cl_2) is formed.



If 1 volume of methane and 3 volumes of chlorine are employed, chloroform or trichlormethane (CHCl_3) is formed.



Lastly, if 1 volume of methane and 4 volumes of chlorine are employed, carbon tetrachloride or tetrachlormethane (CCl_4) is formed.



Test.—When a mixture of 1 volume of the gas and 3 volumes of chlorine is exposed to diffused daylight, chloroform is produced.

ETHANE (C_2H_6)

This paraffin may be considered as dimethyl, $(CH_3)_2$, or ethyl hydride, $(C_2H_5)H$.

Methods of preparation.—1. By the action of sodium on a solution of methyl iodide in ether.



2. By electrolysis of sodium or potassium acetate.

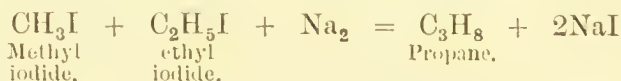


3. By any of the methods 1, 6, 7, employed for the preparation of methane if the corresponding ethyl compound be used instead of the methyl compound—namely, sodium propionate, $C_2H_5CO.ONa$, instead of sodium acetate in 1; ethyl iodide, C_2H_5I , instead of methyl iodide in 6; and zinc ethide, $Zn(C_2H_5)_2$, instead of zinc methide in 7. Ethane is most conveniently *prepared* by 6. A few c.c. of ethyl iodide, mixed with an equal volume of alcohol, are poured on a clean copper-zinc couple placed in a small flask. On gently warming the flask in the water bath, the gas is evolved and may be collected over water.

Properties.—Like methane, ethane is a gas without colour, taste, or smell; it liquefies at -93° and freezes at -123° ; its critical temperature is 35° . The specific gravity ($H=1$) is 1.5; it is therefore very slightly heavier than air. It does not support combustion, but, being richer in carbon, burns with a more luminous flame than methane. It forms substitution products with chlorine in daylight.

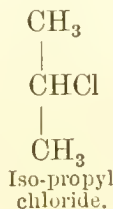
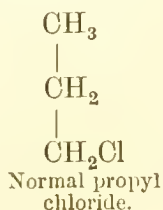
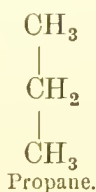
PROPANE (C_3H_8)

This paraffin may be regarded as *methyl ethane*—that is, as being derived from ethane by replacing one H by CH_3 , thus acquiring the constant increment CH_2 . This is really what happens in its preparation; for it can be prepared by the action of sodium on a solution in ether of the iodides of methyl and ethyl (compare method 1, page 436). Ethyl iodide is ethane in which one H has been replaced by I; this I is now withdrawn to combine with the sodium, and its place is filled by methyl, (CH_3). One H of C_2H_6 has therefore been replaced by CH_3 .

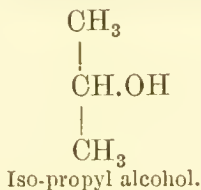
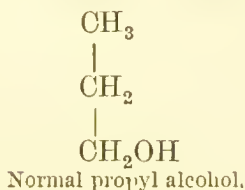


Although similar to them in general properties, propane differs from its predecessors in one important respect. When one H of a methane or ethane molecule is replaced by Cl, OH, or any other radicle, the substitution compound so obtained is always the same, and *no isomeric variety of it is known*. But, when the *same* substitution is effected in a propane molecule, a compound is obtained of which *two, and only two, isomeric varieties are known*. For instance, only one, CH_3Cl , or CH_3OH , has ever been obtained from CH_4 , and only one, C_2H_5Cl , or C_2H_5OH , from C_2H_6 , but from propane, (C_3H_8), *two* kinds of C_3H_7Cl and two kinds of $C_3H_7.OH$ have been obtained and clearly distinguished. From these proved facts we are compelled to infer that some difference exists between the H atoms in propane which does not exist in methane or ethane. An inspection of the graphical formulæ of the three paraffins (page 435) shows that this difference really does exist; for, whereas in methane all *four* H atoms occupy exactly

similar positions, and in ethane all *six* H atoms are also similarly placed, in propane, on the other hand, the *eight* H atoms are not all in exactly similar situations, but may be divided into *two* groups. Six of them belong to the ethane type; that is to say, each of this six is *one of a set of three* which are attached to the same C; the remaining two do not belong to the ethane type, but each is *one of a set of two*, which are attached to the same C whose other two valencies are united to carbon atoms. Substitution for one of the *six* H atoms produces a *normal* propyl derivative; similar substitution for one of the *two* H atoms produces the isomeric variety which is called an *iso*-propyl derivative. Thus we have—

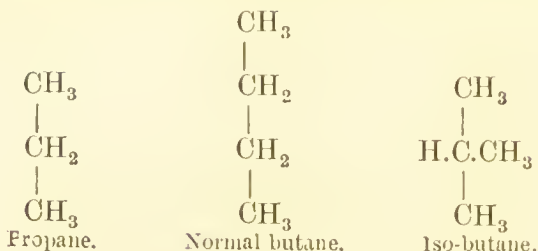


and also



BUTANE (C_4H_{10})

This paraffin is really the methyl derivative of its predecessor, *propane*, and therefore occurs in two varieties, as has been explained in the previous paragraph. They are quite distinct substances. The difference in structure between them and the relation of each to propane is shown in the following graphical formulæ of the three compounds:—



Certain compounds related to butane are of clinical interest, and will be referred to later.

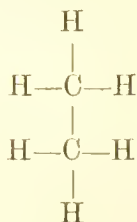
PENTANE (C_5H_{12})

The names of this and higher paraffins indicate the number of carbon atoms in the molecule. Three isomeric pentanes can be derived from the two butanes. All are known. They are normal pentane, iso-pentane, and neo-pentane. The molecule of a neo-paraffin contains one carbon atom to which no hydrogen is directly attached.

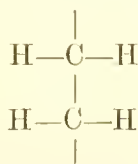
UNSATURATED HYDROCARBONS

There is only one series of saturated hydrocarbons, the paraffins, but there are various series of unsaturated hydrocarbons, because saturation may be more, or less, incomplete. If, for instance, we compare ethylene (C_2H_4) with ethane (C_2H_6) we see that the two carbon atoms in ethylene must have *two* valencies unemployed; we do find, in fact, that it forms its typical compounds by bringing these two valencies into use and so *adding* on *two* Br atoms, or *two* OH groups, etc. Ethylene is, in fact, unsaturated to the extent that a divalent element is, and can therefore function as one. If, however, we compare acetylene (C_2H_2) with ethane (C_2H_6), we see that saturation is still more defective and that acetylene

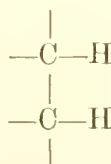
has four unused valencies and can function as a tetrad. Its chemical behaviour confirms this.



Ethane.



Ethylene.



Acetylene.

If we extend this comparison to the general formula we see that since the general paraffin is $\text{C}_n\text{H}_{2n+2}$, the general ethylene hydrocarbon must be C_nH_{2n} , and the general acetylene hydrocarbon must be $\text{C}_n\text{H}_{2n-2}$. We therefore divide unsaturated hydrocarbons into distinct series corresponding to the degrees of unsaturation, and shall at present only illustrate—

- I. The olefine series—general formula C_nH_{2n} ;
- II. The acetylene series — general formula $\text{C}_n\text{H}_{2n-2}$.

I.—OLEFINE SERIES

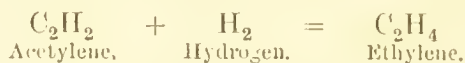
ETHYLENE (C_2H_4)

Known also as *ethene*, *olefiant gas*, and *heavy carburetted hydrogen*:

Modes of preparation.—1. By heating a mixture of one volume of alcohol and four volumes of strong sulphuric acid. The action of the sulphuric acid is simply that of dehydration, or withdrawal of the elements of water from the alcohol; the temperature of the mixture must be above 154° , but the source of heat may be removed when the evolution of gas commences.

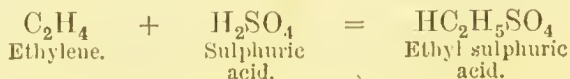


2. By passing acetylene (C_2H_2) through a mixture of zinc and an alkali generating nascent hydrogen.

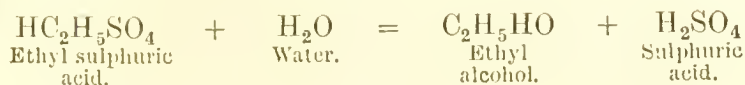


3. Ethylene is produced during the dry or destructive distillation of many organic bodies—coal, for instance—and is present to the amount of about 2 to 5 per cent. in coal gas.

Properties.—A colourless, inodorous, and tasteless gas; its specific gravity is 14, and it is therefore a little lighter than air, liquefies at -103° , and freezes at -169° ; the critical temperature is 9° . It is very slightly soluble in water, and is combustible, but not a supporter of combustion. It burns with a very luminous flame, producing carbon dioxide and water; the luminosity of coal gas when burnt is in great part due to the presence of ethylene in the gas. A mixture of ethylene and oxygen or air explodes on the application of a light. Ethylene is not a direct poison, but it is incapable of supporting life. It unites, by *addition*, with chlorine, bromine, and iodine. Ethylene iodide ($C_2H_4I_2$) is a colourless, crystalline solid, melting at 82° . The bromide ($C_2H_4Br_2$) is also a colourless crystalline solid when cooled below 9° . The chloride is a liquid. All three compounds in the liquid state are of an oily nature, and do not mix with water. To this feature is due the old name of olefant gas (from *oleum*, oil, and *fians*, forming). Ethylene chloride ($C_2H_4Cl_2$) was discovered by some Dutch chemists, and is known as *Dutch liquid*. Ethylene dissolves in strong sulphuric acid, forming ethylsulphuric acid.

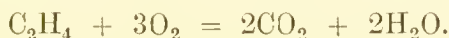


This, when boiled with water, splits up into alcohol and sulphuric acid.



Ethylene is the first member of the olefine series of hydrocarbons; the first four members are gases, the next fourteen liquids.

Tests for ethylene.—The luminosity with which the gas burns, combined with its being inodorous, and the fact that it forms an oily liquid with an equal volume of chlorine, and is absorbed by strong sulphuric acid, constitute the best means for the identification of this gas. Ethylene requires for complete combustion three times its volume of oxygen, thus:

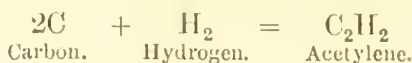


From the volumes of the products obtained we learn the composition of the gas, since we already know the composition of carbonic anhydride and water. *One* molecule of ethylene produces *two* molecules of carbonic anhydride, and therefore must contain *two* atoms of carbon. This one molecule of ethylene also produces two molecules of water vapour, and therefore contains *four* atoms of hydrogen.

II.—ACETYLENE SERIES

ACETYLENE (C_2H_2)

Modes of preparation.—1. By synthesis; if the electric arc is produced in an atmosphere of hydrogen, the two elements will unite at the very high temperature produced, and about 9 per cent. of acetylene is formed. The reaction is endothermic.



2. By passing the vapour of chloroform over red-hot copper.



3. By warming iodoform with a moist copper-zinc couple.



4. By the incomplete combustion of ethylene (C_2H_4), as when the coal gas in a Bunsen burner catches fire at the bottom of the burner; on account of the insufficient supply of air under such conditions, only part of the hydrogen of the ethylene undergoes combustion, acetylene being produced.



5. By the action of alcoholic potash on ethylene dibromide.



6. By the action of water on calcium carbide.



Of late years this method has been largely used for making acetylene for illuminating purposes; 1 lb. of carbide yields about 5 cubic feet of nearly pure acetylene. Care should be taken in its use.

It should not be subjected to a pressure of more than two atmospheres. The calcium carbide (made by heating chalk with charcoal in the electric furnace) should be free from phosphide, or hydrogen phosphide may be produced and fire the acetylene.

Properties. — A colourless gas, possessing, as usually prepared, an unpleasant odour; solidifies at -81° ; its specific gravity ($H = 1$) is 13. It burns with a very bright and (unless the burner has a very small orifice) smoky flame, on account of the large amount of carbon contained in it; if mixed with chlorine it explodes almost instantly.

Acetylene readily forms additive compounds with bromine, forming at first $C_2H_2Br_2$ and finally $C_2H_2Br_4$. In presence of platinum black it unites with hydrogen to form ethane. When passed into an ammoniacal solution of cuprous chloride (page 382), acetylene produces a red precipitate, *cuprous acetylde*, $C_2Cu_2 \cdot H_2O$; when passed into an ammoniacal solution of silver nitrate a white precipitate, $C_2Ag_2 \cdot H_2O$, is produced. This tendency to form metallic acetylides is the most remarkable and characteristic property of the gas. It may therefore be used to identify the gas. It also enables us to separate the gas from a mixture of gases and to recover it in a pure state. If the moist precipitate is collected, and acted on by dilute hydrochloric acid, it is readily decomposed with evolution of the pure acetylene.



The acetylde of copper therefore behaves as if its constitution were $C_2H_2 \cdot Cu_2O$, and this formula is sometimes preferred. Its true constitution is not known. When pure and dry the metallic acetylde is too unstable and explosive to admit of precise investigation.

Constitution.—That acetylene consists of two CH groups (page 443) and *not* of one CH₂ group and

one C atom, thus, $\begin{array}{c} | \\ -\text{C}-\text{CH}_2 \\ | \end{array}$, is inferred (1) from the

fact that such a molecule, in which the two C atoms are unsaturated to different degrees, cannot apparently exist in a free state ; and (2) from the methods of preparation (2) and (3) on page 446, in which acetylene is obtained from chloroform and iodoform respectively, for the molecules of these two compounds contain their carbon and hydrogen in one CH group only.

In favourable circumstances, acetylene polymerises and forms benzene (C₆H₆), an important hydrocarbon, which will be more conveniently considered in a later chapter.

CHAPTER V

ALCOHOLS

Monohydric Alcohols, Primary, Secondary, and Tertiary:
Methyl Alcohol and Derivatives—Ethyl Alcohol
and Derivatives—Higher Homologues of Ethyl
Alcohol. Dihydric Alcohols: Glycol. Trihydric
Alcohols: Glycerol.

ALCOHOLS have already appeared (page 395) as the hydroxides of those positive hydrocarbon radicles which correspond to the positive or metallic elements in inorganic compounds. They therefore correspond to the inorganic bases, and just as those bases differ in valency (page 59) because the elements do, so must alcohols differ in valency because these radicles do. We therefore divide alcohols into—

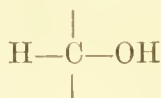
- I. Monovalent, or monohydric, alcohols.
- II. Divalent, or dihydric, alcohols.
- III. Trivalent, or trihydric, alcohols,

and so on, according to the number of alcoholic hydroxyl groups in the molecule of the alcohol.

I.—MONOHYDRIC ALCOHOLS

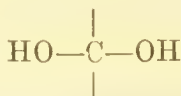
These are the hydroxides of monovalent hydrocarbon radicles, and contain only one alcoholic hydroxyl group in the molecule. They are illustrated by the hydroxyl derivatives of the paraffins already mentioned—e.g. *methyl alcohol* from methane (page 424), *ethyl alcohol* from ethane (page 424), and *normal propyl alcohol* from propane (page 441).

They are all derived from the hydrocarbon by replacing one H atom of a CH_3 group by OH, and therefore contain the class-group CH_2OH . They are *primary* alcohols, and give rise by oxidation to aldehydes and acids. These important changes have already been fully discussed (page 425). In the discussion of propane (page 441) attention was especially directed to the fact that from this hydrocarbon an isomer of each derivative can be obtained by replacing one of the H atoms in the CH_2 group instead of in the CH_3 group. In the case of the hydroxyl derivative, this leads to iso-propyl alcohol (page 441). This is the first member of a series of *secondary* alcohols which must evidently contain the class-group CH.OH , or, graphically—

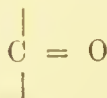


this C atom being connected, in the compound, to two others.

The secondary alcohols do not, on oxidation, lead to aldehydes, but give rise to a new class of compounds called ketones. As before (*see* page 425) we suppose the first stage to be represented by the insertion of an O atom, thus—

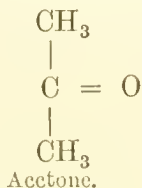
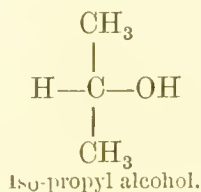


and this by loss of H_2O from the two OH groups (*see* page 61) becomes immediately

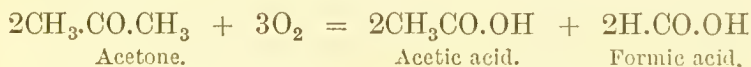


The secondary alcohol has now been transformed to a *ketone*, with the new class-group that characterises

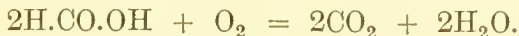
these compounds. While these changes take place in the class-group, the rest of the molecule remains the same. The particular ketone derived from the secondary propyl alcohol is named *acetone*. It has the formula $\text{CH}_3\text{CO.CH}_3$, and is related to the secondary alcohol as shown—



Further oxidation does not, as in the case of aldehydes (page 425), produce a single acid, but apparently interrupts the connection between two C atoms—upon which the existence of the molecule depends—and results in the production of more than one acid, each containing, therefore, a smaller number of carbon atoms in its molecule than the original ketone. Acetone, for instance, gives rise to acetic and formic acids, thus :



but the formic acid may undergo further oxidation to carbonic anhydride and water, thus :



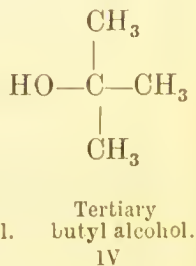
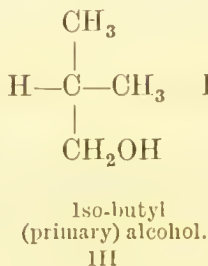
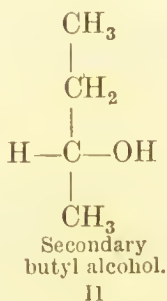
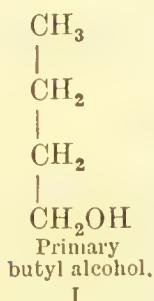
The student must be careful not to confuse *iso* alcohols with *secondary* ones. It is only a coincidence that isopropyl alcohol is a *secondary* alcohol; iso alcohols may also be *primary* or *tertiary*, for there is a *third* variety which we are about to describe. The prefix *iso* in fact only indicates that it is an iso derivative of propane, or obtained from an isoparaffin—e.g. *iso-butane*. Inspection of the formulæ of normal and iso-butane shown on page 442 will

make this point clearer. Normal butane contains a CH_3 group, and therefore gives rise to a primary butyl alcohol (I); normal butane also contains a CH_2 group, and therefore gives rise to a secondary butyl alcohol (II). Neither of these is an *iso*-alcohol.

Iso-butane contains a CH_3 group, and therefore can give rise to a primary alcohol which is *iso*-butyl primary alcohol (III); it contains no CH_2 group, and therefore cannot give rise to a secondary alcohol; but it *does* contain one CH group, and when the H atom of this group is replaced by OH we obtain a third type of alcohol, called a tertiary alcohol. Tertiary butyl alcohol (IV) is the first member of the class which is evidently characterised by the

group $\begin{array}{c} | \\ -\text{C}-\text{OH} \\ | \end{array}$. These tertiary alcohols yield, on

oxidation, neither aldehydes nor ketones, but break down at once into two or more acids, each containing a smaller number of carbon atoms in the molecule than the original tertiary alcohol. Both (III) and (IV) are *iso* alcohols, because derived from *iso*-butane, but neither is secondary.



These four alcohols are all known. They are isomers, having the common molecular formula $\text{C}_4\text{H}_9\text{OH}$, but differ in constitution as shown. They also boil at different temperatures. The primary

(I) boils at 117° , but the primary (III) boils at 107° ; the secondary (II) boils at 100° , while the tertiary (IV) boils at 84° .

Since the general formula of a paraffin is C_nH_{2n+2} , the general formula of a monohydric alcohol derived from it must be $C_nH_{2n+1}.OH$.

We shall now consider more fully the two first members of this series of alcohols, with some of their important derivatives.

ALCOHOLS OF THE $(C_nH_{2n+1}.OH)$ OR METHYL SERIES

METHYL ALCOHOL (CH_3OH)

The formation of this alcohol from inorganic compounds, and ultimately from elements, is rendered possible by the following reactions.

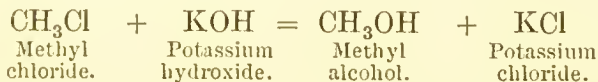
1. H_2S can be prepared from its elements (page 252).

2. CS_2 is prepared from its elements (page 209).

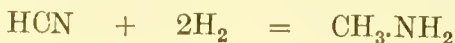
3. CH_4 is prepared from CS_2 and H_2S (page 436).

4. CH_3Cl is prepared from CH_4 and Cl_2 (page 438).

5. When CH_3Cl is heated to 100° for a week, in a closed vessel, with a dilute aqueous solution of potassium hydroxide, methyl alcohol is produced.



The synthesis of methyl alcohol from elements can also be effected thus: Nitrogen is passed over heated carbon in the presence of potassium hydrate, when potassium cyanide is formed; by distillation with dilute sulphuric acid hydrocyanic acid is obtained. This, by the action of nascent hydrogen,



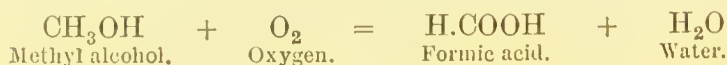
is converted into methylamine (page 427), which by the action of nitrous acid yields methyl alcohol (page 428).



This is an important synthesis, because from methyl alcohol we can easily obtain potassium methyl sulphate (KCH_3SO_4) (page 456), and by heating this salt with potassium cyanide we form methyl cyanide; this by treatment similar to the above yields ethyl alcohol, and so we can ascend the alcohol series.

Pure methyl alcohol may also be prepared from the *oil of winter green*, which is pure methyl salicylate; by distilling this with caustic potash or soda, methyl alcohol is obtained. Impure methyl alcohol, commonly known as *wood spirit* or *wood naphtha*, is obtained by the dry or destructive distillation of wood (*see* page 498); 10 per cent. of this wood spirit mixed with rectified spirit formerly constituted the *methyiated spirit* of commerce. The present methyiated spirit contains coal-tar spirit, which renders it useless for many purposes in the laboratory.

Properties.—Methyl alcohol is a colourless, inflammable liquid (*sp. gr.* .796, *boils* 66°); it produces carbon dioxide and water when burnt. In the pure state it is free from the disagreeable smell possessed by wood spirit. Methyl alcohol is converted by oxidation into formaldehyde, and then into formic acid (*see* page 426); this oxidation may be effected either by dropping methyl alcohol on to platinum black, the occluded oxygen of which oxidises the alcohol, or by distillation with potassium bichromate and sulphuric acid.



The test for methyl alcohol is to convert it by the last-mentioned process into formic acid (for the detection of which *see* page 496).

FORMALDEHYDE (H.CHO)

Is known as a gas or in solution, and is a powerful antiseptic and disinfectant. It is prepared by passing air saturated with the vapour of methyl alcohol through a red-hot tube containing spongy platinum, and condensing the vapour, which yields a solution containing 33 to 44 per cent. of formaldehyde. It is a strong reducing agent.

METHYL CHLORIDE (CH₃Cl)

This may be prepared by exposing equal volumes of methane and chlorine to sunlight (page 438). It may also be prepared by the action of phosphorous chloride on methyl alcohol.



METHYL IODIDE (CH₃I)

This is prepared by the action of phosphorous tri-iodide on methyl alcohol.

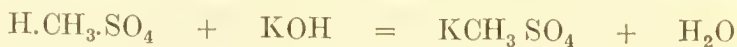


METHYL OXIDE OR METHYL ETHER [(CH₃)₂O]

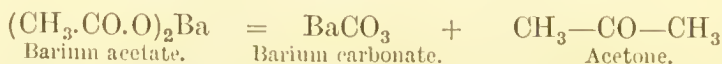
This is prepared by heating a mixture of equal volumes of methyl alcohol and strong sulphuric acid, when it passes over as a colourless gas.

METHYL SULPHURIC ACID (HCH_3SO_4)

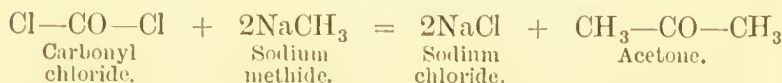
This is prepared by the action of sulphuric acid on methyl alcohol, with moderate heat. It is also called methyl hydrogen sulphate. It acts as a monobasic acid, and reacts with bases to form salts—e.g. potassium methyl sulphate, KCH_3SO_4

DIMETHYL-KETONE, OR ACETONE ($\text{CH}_3\text{—CO—CH}_3$)

This ketone is prepared by the action of dry heat on a metallic acetate; the barium or calcium salt answers well.



It may also be prepared by the action of sodium methide on carbonyl chloride.



Metallic sodium acts upon methyl alcohol as it does upon water, but it is found that only one atom of hydrogen can be replaced by sodium.



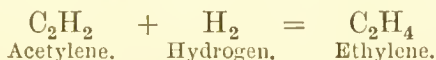
We therefore conclude that one of the atoms of hydrogen is combined differently from the other three. Again, methyl alcohol can be produced by the action of potash upon methyl chloride (CH_3Cl). Now, in this last substance the three atoms of hydrogen must be combined with the atom of carbon, so we conclude that they are similarly combined in methyl alcohol, and we write the formula CH_3OH . This is

confirmed by the action of phosphorus pentachloride, which replaces one hydroxyl group by chlorine (*see* page 235).

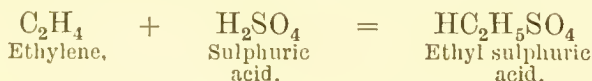
ETHYL ALCOHOL AND ETHYL COMPOUNDS

ETHYL ALCOHOL (C_2H_5OH)

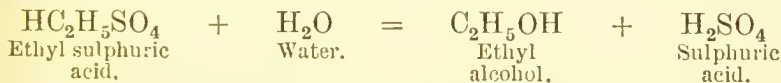
This constitutes the ordinary alcohol of commerce as contained in proof spirit, rectified spirit, absolute alcohol, wines, and beers. It may be prepared by a synthetical process, which is of interest as showing the building up of the alcohol from its elements. To effect this, acetylene is first prepared by direct union of its elements, by the production of the electric arc in an atmosphere of hydrogen; the acetylene (C_2H_2) is then converted into ethylene by nascent hydrogen (sodium amalgam).



The ethylene is then agitated with strong sulphuric acid, which converts it into ethyl sulphuric acid.



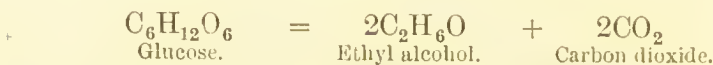
The ethyl sulphuric acid, if distilled with water, yields ethyl alcohol as a distillate.



The various forms of ethyl alcohol met with in commerce are obtained by the fermentation of sugar under the influence of yeast. If a solution of ordinary sugar ($C_{12}H_{22}O_{11}$) is mixed with yeast, and the mixture kept in a covered vessel in a warm place, the cane sugar is first converted into glucose.



The glucose is then decomposed, by the fermentative action of the yeast, into alcohol and carbon dioxide, small quantities of other bodies (such as glycerin succinic acid, etc.) also being produced.



When the fermentative process is finished, the alcohol in a weak state is obtained from the mixture by distillation. This weak spirit is then strengthened by the process known as *fractional distillation*, which consists in distilling it in portions, the greater quantity of the alcohol being contained in the first distillate. It is not possible to remove all the water by the process of fractional distillation; the strongest spirit that can be so obtained is *rectified spirit*, which contains 10 per cent. of water. To prepare *absolute alcohol* from this—that is, alcohol quite free from water—the rectified spirit is mixed with freshly-burnt lime, and allowed to stand for some hours in a closed vessel. The lime unites with the water, forming slaked lime, and the pure or absolute alcohol can then be obtained by distillation. In the preparation of malt alcoholic liquors (beer, stout, and porter), the starch contained in barley is converted by a ferment, *diastase*, which exists in the barley grain, into a mixture of dextrin and a form of sugar known as *maltose* ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$); the latter is extracted with hot water, and the solution, when sufficiently cold, fermented with yeast; the maltose is converted by the yeast into alcohol and carbon dioxide.

Properties.—Ethyl alcohol is a colourless liquid with a faint, pleasant smell, and is readily inflammable, producing, when burnt, carbon dioxide and water. *Proof spirit* contains 49 parts by weight of alcohol in 100 volumes, and is of specific gravity

0·920. *Rectified spirit* contains 90 parts by volume in 100 volumes of alcohol, and is of specific gravity 0·834. *Absolute alcohol* contains no water, is of specific gravity 0·793, and boils at 78·4°. The various wines and beers met with in commerce contain different amounts of alcohol, as shown in the following table :—

Brandy	}	.. From 36 to 60 per cent. by volume.		
Gin				
Whisky				
Port	}	.. About 18 per cent. ,, ,,		
Sherry				
Champagne	..	About 12 per cent.	,,	,,
Claret	}	.. From 10 to 12 per cent. ,, ,,		
Hock				
Beer	From 3 to 6 per cent.	,,	,,

The strength of alcoholic beverages is expressed by the excise as *under* or *over proof*; 25 over proof means that 100 volumes of the spirit will make 125 volumes of proof spirit; 25 under proof indicates that 100 volumes of the fluid contain 75 volumes of proof spirit.

Test for ethyl alcohol.

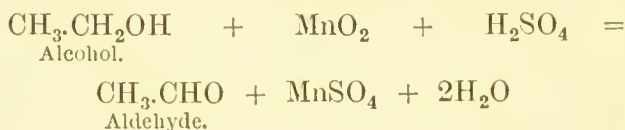
On warming the alcoholic solution with a little aqueous solution of potassium bichromate, acidulated with dilute sulphuric acid, the mixture acquires a green colour and evolves a characteristic fruity odour (of aldehyde).

ACETIC ALDEHYDE, ACETALDEHYDE, OR ALDEHYDE ($\text{CH}_3\cdot\text{CHO}$)

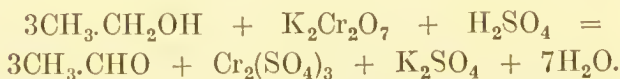
As already explained (page 426), this substance is the result of the initial oxidation of alcohol. It is accordingly prepared by acting on alcohol with an oxidising agent, such as manganese dioxide and sulphuric acid (page 101), or potassium bichromate

and sulphuric acid (page 103). In either case a well cooled mixture of water, acid, and alcohol is made, and cautiously added to the solid peroxide or bichromate, previously placed in a distilling flask connected with an efficient condenser. If necessary, gentle heat may be applied by means of the water bath, but the reaction is an exothermic one, and the student's difficulty is generally not in effecting the production of the aldehyde, but in preventing its too rapid evolution and imperfect condensation. It is a very volatile liquid, boiling a little above room temperature, and the condenser therefore requires to be kept quite cold, and the receiver should be surrounded with ice and salt. The reaction may be thus expressed:

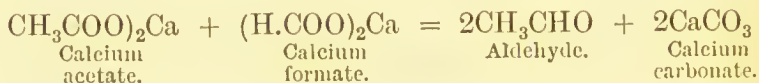
1. With manganese dioxide—



2. With potassium bichromate—



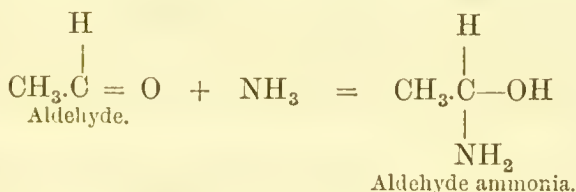
Aldehyde may also be obtained by dry distillation of an intimate mixture of calcium acetate and calcium formate—



Properties.—Aldehyde is a colourless liquid with a peculiar smell, boils at 20.8° , and is very inflammable. Its name is derived from an abbreviation of the expression *alcohol dehydrogenated*, as it is alcohol deprived of part of its hydrogen: By exposure

to the air it absorbs oxygen and becomes converted into acetic acid; reducing agents convert it into alcohol. Acted upon by phosphorus pentachloride, the oxygen atom is replaced by two atoms of chlorine. A polymeric modification of it—viz. *paraldehyde* ($C_6H_{12}O_3$)—is prepared by adding a few drops of concentrated sulphuric acid to aldehyde, when the liquid becomes hot, and, on cooling, crystals of paraldehyde form. When warmed with potassium hydroxide, aldehyde is converted into a yellow or brown mass (*aldehyde resin*), while the solution acquires a characteristic and rather unpleasant odour. Aldehyde is a powerful reducing substance, precipitating silver in the metallic state from ammoniacal solution of silver nitrate. Aldehyde forms several important additive compounds, including these:

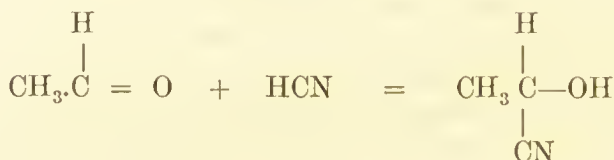
1. When dry ammonia gas is passed into a mixture of aldehyde and ether, the aldehyde combines with the ammonia to form colourless crystals of *aldehyde ammonia*, which are decomposed by dilute acids, liberating aldehyde, which is thus purified.



2. Shaken with a concentrated solution of sodium bisulphite, an additive compound is formed from which the aldehyde may be recovered by warming with solution of sodium carbonate.



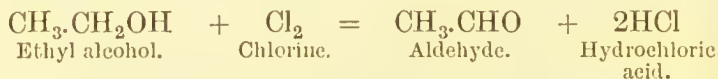
3. A *cyanhydrin* formed by additive combination with hydrocyanic acid (prussic acid).



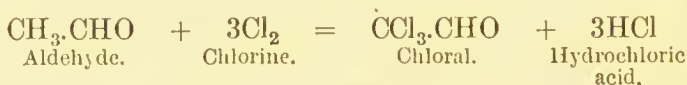
CHLORAL, OR TRICHLORALDEHYDE ($\text{CCl}_3\text{.CHO}$)

This body constitutes what is commonly known as chloral, the hydrate of which is *chloral hydrate*, prepared in the way described on page 463. Chloral is prepared by the prolonged action of chlorine upon absolute alcohol. The reaction may, for the sake of simplicity, be regarded as taking place in the two following stages, though it is really more complex, intermediate compounds of alcohol and aldehyde being temporarily formed.

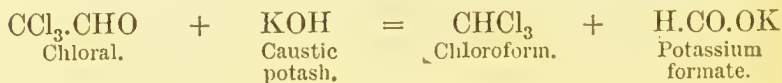
1. Chlorine converts the alcohol into aldehyde.



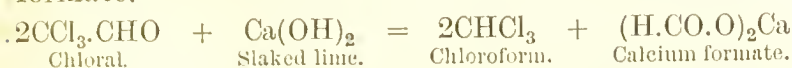
2. Chlorine replaces all the hydrogen of the CH_3 group.



Properties.—Chloral is a heavy liquid, with an extremely pungent, irritating odour. It is converted by the action of alkalis into chloroform and a formate of the alkali metal. Thus, with caustic potash it yields chloroform and potassium formate.



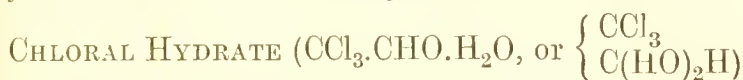
With slaked lime it yields chloroform and calcium formate.



Like aldehyde, ehloral is a strong reducing agent, and immediately reduces ammoniacal silver nitrate solutions.

Just as aldehyde is oxidised by nitric acid to acetic acid, so chloral or trichloraldehyde is oxidised by nitric acid to trichloroacetic acid ($\text{CCl}_3\cdot\text{COOH}$).

Chloral, when mixed with water, produces a crystalline mass of *chloral hydrate*.



This body, as just mentioned, is prepared by the action of water on ehloral. It is a white crystalline solid, with a very faint odour of the liquid ehloral attached to it. It dissolves readily in water, and the aqueous solution both reduces silver nitrate and evolves chloroform when warmed with potash. It is largely used in medicine as a hypnotic, and has been stated to be decomposed by the sodium carbonate of the blood into ehloroform, though it is very doubtful whether such a decomposition takes place.

Chloral hydrate is decomposed by contact with caustic alkalies into chloroform and formate of the alkali metal. It is therefore incompatible with alkalies, and should never be prescribed with them in medicine.

CHLOROFORM (CHCl_3)

This body is actually a derivative of methane (CH_4), from which it may be obtained by the action of chlorine (*see* page 438); but since all the chloroform of commerce really results from the decom-

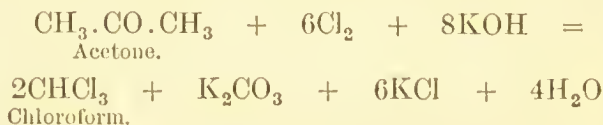
position of chloral, it is more convenient to describe its preparation in the present section. Chloroform, on the commercial scale, is prepared by distilling a mixture of alcohol or acetone, water, chlorinated lime (bleaching powder), and slaked lime. The formation of chloroform takes place in the three following stages:—

1. The chlorinated lime (CaOCl_2) oxidises the alcohol to aldehyde (page 462).

2. The aldehyde is then converted, by some of the chlorine of the chlorinated lime, into chloral (page 462).

3. The chloral is then decomposed by the slaked lime into chloroform and calcium formate, the chloroform distilling over (page 463).

Chlorine also converts *acetone* to chloroform in presence of alkalis—e.g. caustic potash.

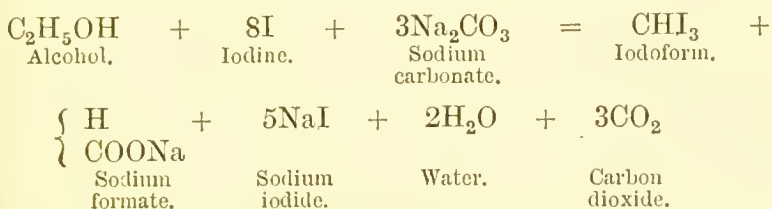


Properties.—The specific gravity of chloroform is 1.5. The medicinal chloroform contains a minute amount of alcohol, and is of specific gravity 1.497; it boils at 61° . It is a thin colourless liquid, with a sweetish taste and a pleasant odour. It is readily soluble in alcohol and ether, and slightly so in water (*aqua chloroformi*). It is difficult to kindle, and burns with a greenish smoky flame. When allowed to stand exposed to light and air it takes up an atom of oxygen, forming the poisonous phosgene gas (COCl_2) and HCl .

iodoform (CHI_3)

This body is analogous in constitution to chloroform,[†] and is produced in a similar way;

that is, by the action of *iodine* (in place of chlorine) on alcohol or acetone. It is prepared by warming together sodium carbonate, alcohol, water, and iodine. About 4 grm. of the crystallised carbonate is dissolved in 25 c.c. of hot water, and to the solution (when not above 70°) 5 c.c. of alcohol is added, and then solution of iodine in potassium iodide, gradually, as long as the colour of the iodine continues to disappear. The yellow precipitate of iodoform is filtered off, washed with cold water, and finally recrystallised from hot alcohol.



The production of iodoform constitutes a very delicate test for alcohol or acetone. It may be made still more delicate by the subsequent addition of a little aniline or other primary amine. On then warming again with a little caustic potash, if iodoform has been produced, a carbamine will be formed (*see* page 432), and can be more easily identified than the iodoform itself. Iodoform occurs in yellow, shiny scales, almost insoluble in water, but soluble in alcohol and ether. It has a characteristic penetrating and somewhat unpleasant smell.

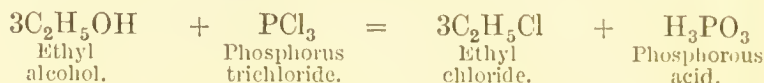
BUTYL CHLORAL ($\text{CH}_3\text{.CHCl.CCl}_2\text{.CHO}$)

A hydrate of this body (*butyl chloral hydrate*) is used in medicine, and is still sometimes called *croton chloral*, which was the original name erroneously applied to it. It is a body corresponding in its constitution to ordinary chloral, since it is trichlorobutyl-aldehyde—that is, it is butyl aldehyde from

the molecule of which three atoms of hydrogen have been displaced by three atoms of chlorine. It is a product of the action of dry chlorine on ordinary aldehyde in the cold.

ETHYL CHLORIDE (C_2H_5Cl)

This substance is formed by the action of phosphorus trichloride on ethyl alcohol.



It is prepared by the action of dry hydrochloric acid gas on absolute alcohol. Anhydrous zinc chloride is present to take up the water formed and prevent the reaction from being reversed.



The chloride is a volatile liquid, boiling at 12° , and burns with a greenish flame. It has had a considerable vogue as a dental anæsthetic.

The presence of about 25 per cent. of this substance seems to improve the anæsthetic action of pure chloroform.

ETHYL IODIDE (C_2H_5I)

This can be prepared by the action of phosphorus tri-iodide on ethyl alcohol.



As a rule, the iodide is made by the direct action of phosphorus and iodine on the alcohol: 100 gm. of iodine is added gradually to 50 gm. of alcohol and 10 gm. of amorphous phosphorus, the mixture allowed to stand, and then distilled on the water bath. The distillate is shaken with dilute caustic

potash, washed, dried by standing over fused calcium chloride, and redistilled; it is a colourless liquid, nearly twice as heavy as water, and boils at 72° . Sodium ethoxide (NaOC_2H_5) converts it to

ETHYL ETHER $[(\text{C}_2\text{H}_5)_2\text{O}]$

This is commonly known as *ether* or *sulphuric ether*. It is the oxide of ethyl, but the process for its preparation will be rendered more intelligible by regarding it as ethyl alcohol partially dehydrated. Thus, if from two molecules of ethyl alcohol one molecule of water be abstracted, ether is obtained.

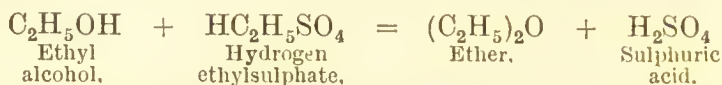


The process for preparing ether on a commercial scale, which is known as the *continuous etherification process*, consists in partially dehydrating ethyl alcohol by means of strong sulphuric acid. This process is carried out (Fig. 45) by distilling a mixture of sulphuric acid and rectified spirit, the latter being in excess. The ether, as it is formed, distils over, the sulphuric acid remaining in the retort, and therefore, to prevent the sulphuric acid from being in excess, it is necessary that as fast as the ether distils over, more alcohol should be run into the retort, so that the temperature of the boiling mixture remains between 140° and 145° . If this is effected the process becomes a continuous one; hence its name. The sulphuric acid withdraws the water from the alcohol not directly, but indirectly, in the two following stages:—

1. The sulphuric acid first forms with the alcohol, hydrogen ethylsulphate (sulphovinic acid or ethylsulphuric acid).



2. This ethyl sulphuric acid then reacts with more alcohol, forming ether and sulphuric acid.



The sulphuric acid, reproduced in reaction 2, is able to repeat reaction 1 on a fresh charge of

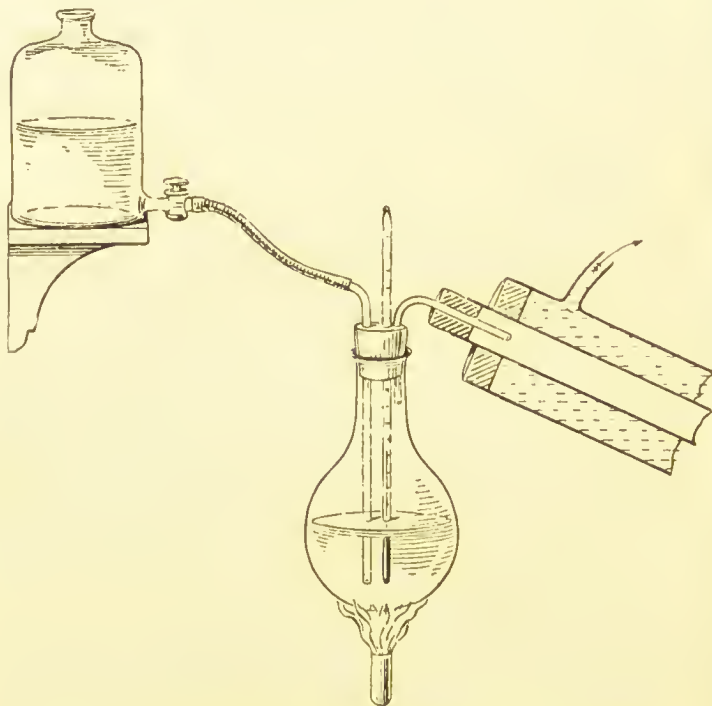


Fig. 45.—Apparatus for the continuous ether process.

alcohol; thus the cycle is *continuous* until in time the water formed in 1 dilutes the sulphuric acid to a point at which it becomes too weak to effect the reaction.

It is therefore essential to the production of ether by this process that the alcohol should be kept in excess; otherwise, if the sulphuric acid

become in excess, it will completely dehydrate the alcohol, forming ethylene or olefiant gas (*see* page 443).

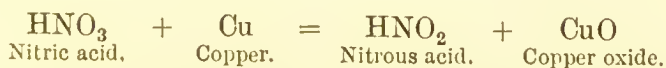


Properties.—The ether obtained by the process just given contains about 8 per cent. of alcohol, from which it can be purified by agitating with water; on standing, the ether rises to the surface of the water, leaving the alcohol in solution; the ether is then removed from the surface of the water, and distilled with some freshly-made quicklime to free it from the little water that it contains.

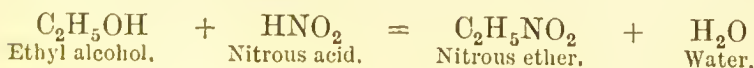
Pure ether is a colourless, transparent, very mobile liquid, with a characteristic fragrant smell, and extremely volatile. Its specific gravity is 0.720; it boils at 35°. It is very combustible, producing carbon dioxide and water when burnt. When dropped on the hand it occasions a sharp sensation of cold from its rapid evaporation. Ether is miscible with alcohol in all proportions, but in water it is soluble only to a very small extent. It dissolves many fats, oils, resins, and alkaloids.

ETHYL NITRITE, OR NITROUS ETHER ($\text{C}_2\text{H}_5\text{NO}_2$)

This ester, mixed with aldehyde, alcohol, and other substances, is contained in sweet spirits of nitre (*spiritus ætheris nitrosi*, B. P.), which is made by distilling together rectified spirit, copper turnings, sulphuric acid, and nitric acid. The copper reduces the nitric acid to nitrous acid.



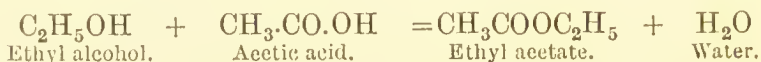
The nitrous acid then acts upon the alcohol, forming nitrous ether.



The preparation of nitrous ether by this process constitutes a fairly good test for alcohol, the peculiar apple-like odour of nitrous ether being readily recognised.

ETHYL ACETATE, OR ACETIC ETHER ($\text{CH}_3\text{CO.OC}_2\text{H}_5$)

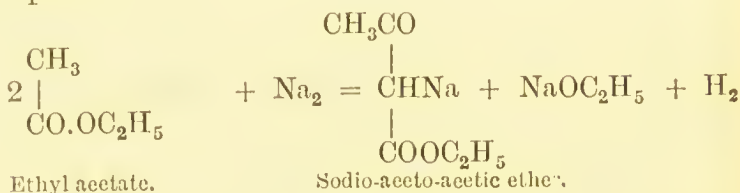
This is prepared by adding a *cold* mixture of strong sulphuric acid and strong alcohol, in equal volumes, to *fused* sodium acetate placed in a distilling flask, and gently warming the mixture on a water bath. Acetic acid is liberated and acts upon the alcohol, producing ethyl acetate.



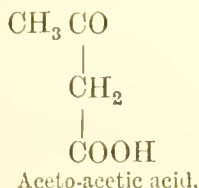
Ethyl acetate is a colourless liquid boiling at 77° ; it has an agreeable fruity odour. Its formation by heating sulphuric acid with alcohol and an acetate is often used as a test for an acetate. It is a typical *ester*, and when heated with caustic soda is converted into alcohol and sodium acetate.



With sodium the pure ester forms an important compound.

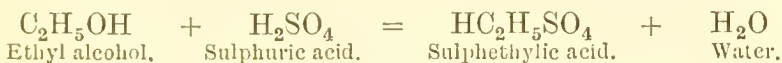


The sodium in this compound can be replaced by hydrogen by the action of acetic acid, and we then obtain the ethyl ester of *aceto-acetic acid*. This acid is sometimes present in diabetic urines. It has evidently the formula—



HYDROGEN ETHYL SULPHATE OR SULPHOVINIC ACID ($\text{HC}_2\text{H}_5\text{SO}_4$)

Prepared by warming a mixture of equal parts of ethyl alcohol and sulphuric acid to 100° for some time.

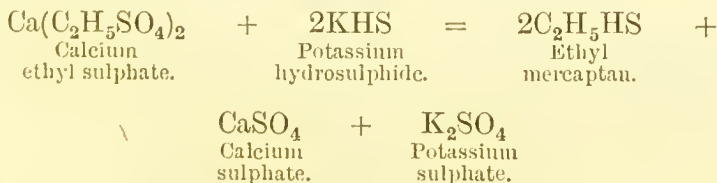


It can also be prepared by absorbing ethylene in strong sulphuric acid.

It is a thick, sour liquid; when boiled with water it yields alcohol, heated with alcohol it gives ether, heated alone it yields ethylene. It still retains half the hydrogen of the sulphuric acid, and acts as a monobasic acid therewith, forming salts, e.g. potassium ethyl sulphate ($\text{K.C}_2\text{H}_5.\text{SO}_4$) (see page 454).

ETHYL HYDROSULPHIDE, OR ETHYL-MERCAPTAN ($\text{C}_2\text{H}_5\text{HS}$)

Prepared by distilling a mixture of potassium hydrosulphide and calcium ethyl sulphate.



It is a liquid with an extremely unpleasant, nauseating odour.

HIGHER HOMOLOGUES OF ETHYL ALCOHOL

PROPYL ALCOHOL (C_3H_7OH)

The two isomeric varieties of this alcohol have already been sufficiently described (*see* pages 441, 450).

BUTYL ALCOHOL (C_4H_9OH)

The four butyl alcohols have also been sufficiently considered (*see* page 452).

AMYL ALCOHOL ($C_5H_{11}OH$)

Eight possible isomerides of this alcohol can be derived from the three pentanes (page 442). Two are present in the *fusel oil* obtained in the preparation of ordinary alcohol from the different forms of starch (*Lat. amyllum*, starch).

Properties.—Commercial amyl alcohol is an oily, colourless liquid having a peculiar unpleasant odour. It is not appreciably soluble in water, but floats on the surface of it like an oil; hence its name *fusel oil*. When oxidised it yields *valerianic acid*.

AMYL NITRITE ($C_5H_{11}NO_2$)

This compound is prepared by a process similar to that employed in the preparation of ethyl nitrite, namely, by distilling a mixture of amyl alcohol, copper turnings, sulphuric and nitric acids.

AMYL ACETATE ($CH_3COOC_5H_{11}$)

This substance is prepared by distilling amyl alcohol with sodium acetate and sulphuric acid. It constitutes the *jargonelle-pear essence*.

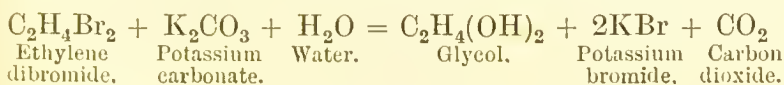
II.—DIHYDRIC ALCOHOLS

These are hydroxides of the divalent hydrocarbon radicles, and therefore contain two hydroxyl groups

in the molecule. Several of them exist under the name of *glycols*, so named from their sweet taste, but as they are of no importance in medicine, a brief description of one of them only will be given here.

ETHYLENE GLYCOL [$C_2H_4(OH)_2$]

This is prepared by acting on ethylene with bromine to form ethylene dibromide ($C_2H_4Br_2$), and then decomposing with aqueous potassium carbonate,

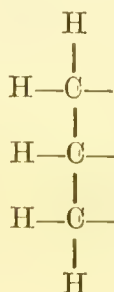


The constitutional formula is $\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$; The compound is therefore a divalent *primary* alcohol, and leads ultimately on oxidation to a dibasic acid

$$\begin{array}{c} COOH \\ | \\ COOH \end{array}, \text{ oxalic acid.}$$

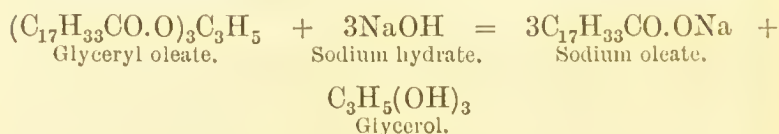
III.—TRIHYDRIC ALCOHOLS

These are hydroxides of the trivalent hydrocarbon radicles, and therefore contain in the molecule three hydroxyl groups. Only one of them is employed in medicine, viz. *glycerine* or *glycerol*. This is the hydroxide of the trivalent radicle *glyceryl* (C_3H_5)''', or, graphically—

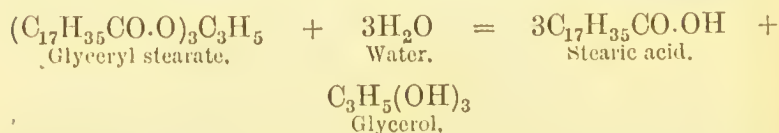


GLYCERINE OR GLYCEROL [$\text{C}_3\text{H}_5(\text{OH})_3$]

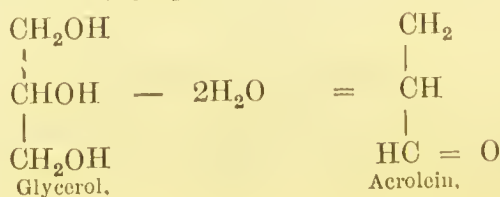
Most fats and oils are compounds of glyceryl with the higher fatty acids. When these fats and oils are saponified by boiling with caustic soda, the radicle (C_3H_5), displaced by the sodium, combines with three hydroxyl groups to form glycerol [$\text{C}_3\text{H}_5(\text{OH})_3$], whilst the sodium combines with the radicle of the fatty acid to form a soap, thus :



Glycerol is more conveniently prepared by decomposing melted suet (glyceryl stearate) by means of superheated steam, when the glycerol and stearic acid are carried over in the current of steam, the stearic acid setting to a solid, and the glycerol, diluted with the condensed steam, being obtained as a liquid.



Properties.—Glycerol is a colourless and very viscid liquid, of specific gravity 1.27, which boils at 290° . It has a very sweet taste and mixes with water in all proportions. When heated by itself or with bisulphate of potash (HKSO_4) it decomposes, losing the elements of water and yielding a substance *acrolein*, ($\text{C}_3\text{H}_4\text{O}$).

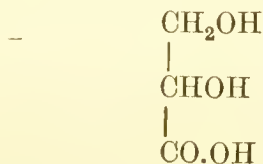


Acrolein is the aldehyde of an unsaturated alcohol (*allyl alcohol*), and has an intensely pungent and characteristic odour. This reaction therefore provides a good test for glycerol.

Glycerol treated with a mixture of strong nitric and sulphuric acids forms *nitroglycerin* [$C_3H_5(NO_3)_3$], a heavy, oily liquid, which produces by percussion a terrible explosion; in its liquid form it is very dangerous to handle, and is, therefore, for blasting and other purposes, made into *dynamite*, which consists of porous silica, in the form of infusorial earth, saturated with nitroglycerin. Ordinary dynamite usually consists of 75 parts of nitroglycerin and 25 parts of silica. Tablets of chocolate containing $\frac{1}{100}$ gr. of nitroglycerin are used in medicine (*tabellæ trinitrini*).

The established name *nitroglycerin* is unfortunately somewhat misleading, for the substance is not really a *nitro* compound, like *nitro-ethane* (page 433). It is really *glyceryl trinitrate*, the *normal* salt (page 66) of *glycerol* and *nitric acid*.

When carefully oxidised with dilute nitric acid, glycerin can be oxidised to glyceric acid, a non-explosive substance—

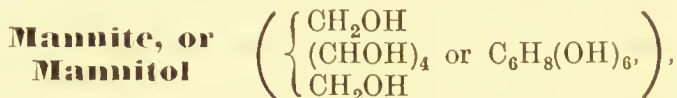


CHAPTER VI

POLYHYDRIC ALCOHOLS—CARBOHYDRATES— GLUCOSIDES

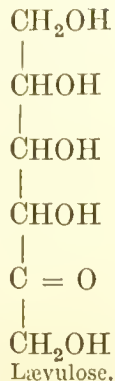
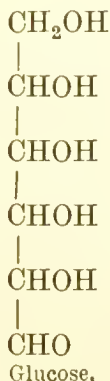
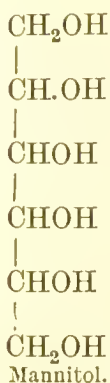
Mannite — Starch — Glysogen — Dextrin — Cellulose — Cane
Sugar — Milk Sugar — Maltose — Glucose — Lævulose —
Glucosides.

THE **polyhydric alcohols** have become, of late years, of great theoretical importance, in consequence of their close connection with glucose, lævulose, and other sugars. The most interesting in this connection is



a hexhydric alcohol found in manna, the dried sap of a species of ash ; it is colourless, crystalline, and somewhat sweet ; it can be formed artificially by reducing either glucose or lævulose with sodium amalgam.

The molecule of mannitol has the class-group of a *primary* alcohol (page 425), which can be oxidised to the aldehyde group ; it has also the class-group of a *secondary* alcohol (page 450), which can be oxidised to the ketone group. The molecule of glucose contains the aldehyde group, and that of lævulose contains the ketone group. It is only natural, therefore, that these two sugars should form mannitol when *reduced*. A comparison of the graphical formulæ of the three bodies will make this important relationship clear.



THE CARBOHYDRATES

These substances owe their name to the old idea that they were compounds of carbon with water; they are really compounds of carbon, hydrogen, and oxygen, in which the atoms of hydrogen are (as in water) twice as numerous as the atoms of oxygen. Those that need be considered here can be conveniently divided into three chief groups:

I. The amylons.

Starch, and its isomers (dextrin, cellulose, etc.). These bodies are not sugars themselves, but, on hydrolysis, they produce sugars. They have the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$.

II. The dihexons.

Cane sugar, and its isomers (milk sugar, malt sugar, etc.). These bodies are sugars having the formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, but, on hydrolysis, they yield one or more different sugars having the formula $\text{C}_6\text{H}_{12}\text{O}_6$.

III. The hexoses.

Glucose, and its isomers (lævulose, etc.). These bodies are sugars having the formula $C_6H_{12}O_6$, and do not, on hydrolysis, yield any different sugar.

I.—AMYLONS

STARCH ($C_6H_{10}O_5$)

Starch is contained in certain roots, seeds, soft stems, potatoes, and various grains, such as wheat, maize, etc. Arrowroot and rice contain considerable quantities of starch. Starch is prepared from roots or seeds by crushing them and placing them upon a sieve or strainer, through which water is flowing. The water mechanically carries the starch through the sieve, leaving fibrous and cellular substances behind. The water is then allowed to stand, and the starch deposits as a white sediment. The water is afterwards poured off, and the sediment dried. Starch may be prepared from wheat and other flours by placing the flour in a muslin or calico bag and wringing it out several times with water, when the starch is mechanically carried away by the water, a sticky substance, gluten, being left in the bag.

Properties.—The different starches are white powders, which, when examined under the microscope, are seen to consist of granules, the granules of the various starches differing in size and shape. Starch is insoluble in cold water, the granules being unaffected by it, but in hot water the granules break up, being in part dissolved and in part remaining in suspension, forming what is called “decoction or mucilage of starch.” Starch, as employed for laundry purposes, is coloured a light-blue with indigo, which is introduced in order to neutralise the faint

yellow colour of recently-washed linen. If a solution of free iodine is added to a cold decoction of starch, a dark-blue colour, due to a molecular compound of iodine and starch, is developed. If heat be applied to the blue liquid, the blue colour disappears, owing to the dissociation of the starch and iodine by the heat. If the heat be quickly withdrawn, the blue colour reappears on cooling. A solution of starch does not reduce an alkaline copper solution when boiled with it. If starch is boiled with dilute sulphuric acid, it is first converted into dextrin and then, by assimilation of water, into grape sugar. Starch is also converted into grape sugar under the influence of certain ferments, such as ptyalin in saliva, the pancreatic ferments in pancreatic juice, etc. Diastase, the ferment in barley, converts starch into a mixture of dextrin and maltose.



This is the first step in brewing.

Test. — The blue colour produced by a solution of free iodine constitutes an extremely delicate test for starch.

GLYCOGEN ($\text{C}_6\text{H}_{10}\text{O}_5$)

This substance, which is an isomer of starch, is found in the livers of man and animals. It is prepared by finely chopping up fresh liver and boiling it with water, which dissolves out the glycogen; from this solution it is precipitated by the addition of alcohol.

Properties. — Glycogen is a white powder, soluble in water, in which it forms an opalescent solution. A solution of free iodine gives a mahogany-brown colour to a solution of glycogen; it is readily converted into grape sugar by contact with certain ferments.

DEXTRIN $(C_6H_{10}O_5)_n$

This substance is prepared from starch either by baking it in an oven, or by boiling it with dilute sulphuric acid, or by the action upon it of ferments such as yeast and diastase. The first-mentioned method is the best, as by the other methods the dextrin is quickly converted into grape sugar.

Properties.—Dextrin is a whitish powder, readily soluble in cold water, in which it forms a sticky or mucilaginous solution. It is commonly employed under the name of *British gum*. Commercial dextrin gives with a solution of free iodine a mahogany-brown colour, which disappears on the application of heat, and does not reappear on cooling; thus it is distinguished from glycogen.

CELLULOSE $(C_6H_{10}O_5)_n$

This substance is also called *lignin*. It is obtained in its purest form as linen, cotton, cotton-wool, Swedish filter-paper, etc. Cellulose is insoluble in both cold and boiling water.

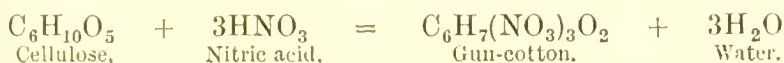
When treated with solution of caustic soda, cellulose undergoes a marked change, shrinking, etc.; this treatment is known as *mercerisation*. Mercerised cotton is largely used at the present day as a substitute for silk. When treated with nitric acid, cellulose forms nitrates; the two which are most important are—

Pyroxylin or dinitrocellulose $[C_6H_8(NO_3)_2O_3]$.—This is prepared by steeping cellulose in a mixture of sulphuric and nitric acids, the strong sulphuric acid being employed to absorb the water produced by the action of the nitric acid on the cellulose.



This substance, dissolved in a mixture of alcohol and ether, constitutes *collodion*, which is employed for producing a covering or artificial skin to abrasions, etc., of the skin.

Gun-cotton, or trinitrocellulose [$C_6H_7(NO_3)_3O_2$].—This substance is prepared by steeping cellulose in the strongest sulphuric and nitric acids.



This is the ordinary gun-cotton employed for blasting purposes and in gun-cotton cartridges. It is an explosive in that it contains sufficient oxygen for the combustion of the carbon and hydrogen contained in it. The explosion of it produces large volumes of the two oxides of carbon, steam and nitrogen, which are, in addition, greatly expanded by the heat produced by the chemical decomposition. It is the sudden production and violent expansion of these gases that cause the destruction produced by gun-cotton when exploded with a detonator; it is a curious fact that if gun-cotton be lighted with a match it burns away rapidly without exploding; it requires a detonation to develop its destructive force.

If a piece of white filter paper be dipped in a cold mixture of 2 volumes of strong sulphuric acid with 1 volume of water for a few minutes, and then thoroughly washed, it is converted into a substance like parchment, and is known as *parchment paper*, largely used for wrapping and for diffusion experiments.

Cellulose gradually dissolves in strong sulphuric acid, and the solution, when diluted and boiled, is found to contain dextrin and grape sugar.

II.—DIHEXONS

CANE SUGAR ($C_{12}H_{22}O_{11}$)

This sugar exists in the sugar cane, date, beet-root, and in the sap of the sugar maple. It is extracted from the sugar cane by crushing the canes in order to squeeze out the juice, to which is then added some slaked lime; the mixture is boiled, and the mechanical impurities are allowed to settle; the liquor, poured off from these impurities, is concentrated by evaporation and set aside to cool, when crystals of *raw or brown sugar* settle out, the viscid mother liquid constituting *molasses*. To obtain the *white or loaf sugar*, the brown sugar is dissolved in water, and some serum of blood and a little slaked lime are added; the liquid is heated, and allowed to stand, when the coagulum produced from the serum of blood settles down, carrying with it impurities. The solution is filtered through animal charcoal to decolorise it, and is evaporated to a syrup, which is poured into conical moulds, within which, on cooling, the white or loaf sugar crystallises. In all modern works the sugar syrup is evaporated in large copper boilers, from which the air has been partially removed, known as *vacuum pans*. In these pans the syrup boils at 65.5° , its boiling-point being lowered by the vacuum about 45° .

Properties. — Cane sugar is readily soluble in both cold and hot water; its solution does not reduce an alkaline copper solution. Nitric acid first converts it into saccharic acid $[COOH(CHOH)_4COOH]$, and then into oxalic acid. It combines with alkalis and with lime to form soluble saccharates. If boiled with dilute sulphuric acid, water is assimilated, and invert sugar is formed, which is a mixture of dextrose and lævulose.



This hydrolysis is also effected by a ferment (invertin) present in ordinary yeast. Another ferment (zymase) present in the yeast decomposes the invert sugar into alcohol and carbon dioxide. If solid cane sugar is carefully heated, a reddish-brown liquid is obtained, which is *burnt sugar* or *caramel*.

Tests.—Cane sugar is easily charred by strong sulphuric acid; it gives a red colour and then a brown precipitate when boiled with strong hydrochloric acid; it does not reduce an alkaline copper solution.

MILK SUGAR, OR LACTOSE ($\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$)

This sugar is contained in milk, from which it may be prepared by precipitating the curds by the addition of rennet or some acid, filtering, and evaporating the clear whey to a low bulk, when the milk sugar crystallises out on cooling.

Properties.—Milk sugar is less soluble in water than any of the other sugars, and also less sweet. It does not undergo fermentation in contact with yeast, or only after a very long time; in contact with the ferment *Penicillium glaucum* it undergoes lactic-acid fermentation; it is this conversion of milk sugar into lactic acid which is the cause of the souring of milk when exposed to the air, the spores of *Penicillium glaucum* being always present in the air, and settling on the exposed surface of the milk. When boiled with dilute acids, lactose is hydrolysed into a mixture of galactose and dextrose. Strong nitric acid oxidises lactose into mucic and saccharic acids.

Tests.—A solution of milk sugar reduces Fehling's

solution when boiled with it, and in this respect it resembles glucose. It can be distinguished from glucose, in the solid state, by its being so much less soluble in water, and in solution by not undergoing fermentation in contact with yeast; whereas a solution of glucose readily ferments in contact with yeast when the mixture is left in a warm place.

MALTOSE ($C_{12}H_{22}O_{11}, H_2O$)

This sugar is obtained by the action of diastase on starch, and gives to malt its sweet taste; it crystallises in needles which are readily soluble in water. It ferments readily with yeast. Boiled with dilute sulphuric acid it is completely hydrolysed to glucose. It reduces an alkaline solution of copper, but only to two-thirds the extent of an equal weight of glucose.

III.—HEXOSES

GLUCOSE, DEXTROSE, GRAPE SUGAR ($C_6H_{12}O_6$,
and see page 477)

This sugar occurs in grapes, honey, and diabetic urine; it can be extracted from any of these sources, and it can be prepared by heating cane sugar with dilute sulphuric acid, when it is obtained mixed with laevulose, or by boiling maltose or starch with dilute acid. It is less sweet, less soluble in water, and more difficult to crystallise than cane sugar; it ferments readily with yeast, forming alcohol and carbon dioxide. Its constitutional formula is known, and it has been prepared artificially from formaldehyde and from glycerin. It is obvious from its formula that it is an aldehyde, as it contains the characteristic group CHO; it is therefore a reducing substance, and readily reduces ammoniacal silver nitrate solu-

tions. Nitric acid converts it first into saccharic acid (*see* page 482), and ultimately into oxalic acid



Tests. — Glucose does not blacken when mixed in the cold with strong sulphuric acid. It reduces an alkaline solution of copper. This reduction test can be applied in two forms: (1) *Trommer's* test. To a small quantity of 5 per cent. solution of copper sulphate add grape sugar and then caustic potash drop by drop until a clear dark-blue solution is obtained; on heating this solution, the blue colour disappears and a precipitate, first yellow, then red, is obtained. The cupric salt is reduced by the glucose to yellow cuprous hydrate, which is ultimately converted into red cuprous oxide. (2) *Fehling's* test. This consists of two solutions, one containing 34.6 gm. of crystallised copper sulphate in 500 c.c. of water; the other, 173 gm. of Rochelle salt and 60 gm. of caustic soda in 500 c.c. of water. These solutions are mixed in equal volumes to make *Fehling's* solution.

For analytical purposes a little of the test solution is diluted with about four times its volume of water, and boiled. The addition to the clear, blue liquid of a few drops of a glucose solution will then effect the reduction described in the previous test. Ten cubic centimetres of the mixed solutions is reduced by .05 gm. of glucose.

Dextrose quickly reduces Barfoed's reagent (4.5 gm. of copper acetate in 100 c.c. of water and 0.2 c.c. of 50 per cent. acetic acid), maltose and lactose do not.

Glucose solutions rapidly acquire a dark-brown colour when boiled with an aqueous solution of potassium hydroxide.

LÆVULOSE, OR FRUIT SUGAR ($C_6H_{12}O_6$, and
see page 477)

This is an isomer of ordinary grape sugar or dextrose; it is a ketone. It occurs in small quantities in honey, and in many fruits mixed with dextrose. It is distinguished from dextrose by its solution turning a ray of polarised light to the left, whereas a solution of dextrose turns it always to the right. It is best prepared by the inversion of cane sugar. This is effected by adding to the sugar solution one-tenth of its volume of strong HCl and then heating the mixture to 70° for ten minutes, when a mixture of dextrose and lævulose is obtained.



To separate the two sugars advantage is taken of the fact that they both form compounds with lime, the dextrose-lime compound being soluble, while the lævulose-lime compound is insoluble. To the solution of the two sugars slaked lime is therefore added, and the mixture filtered; on passing carbon dioxide through the filtrate, the lime is precipitated as calcium carbonate, and the glucose is left in solution. If the insoluble lævulose-lime compound is suspended in water and carbon dioxide passed through, calcium carbonate is precipitated, and the lævulose, in a pure state, is left in solution.

Tests.—Lævulose reduces Fehling's solution in a manner similar to dextrose, but is distinguished from dextrose, as previously mentioned, by its action on polarised light.

ACTION OF SUGAR SOLUTIONS ON POLARISED LIGHT

When a ray of polarised light passes through a solution of a sugar, it is twisted to the right or the

left according to the nature of the sugar, and to a greater or less extent according to the strength and depth of the solution through which the ray passes. Thus, solutions of cane sugar, milk sugar, maltose, and dextrose or glucose twist the ray of polarised light in the direction in which the hands of a watch rotate—i.e. to the right, and are called *dextrorotatory substances*. Lævulose or fruit sugar twists the ray to the left, and is called a *lævorotatory substance*.

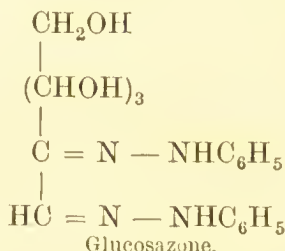
The specific rotation of lævulose is greater than that of dextrose; the rotation of the mixture *invert sugar* is therefore lævo, while that of the cane sugar before inversion is dextro. The rotation has therefore in a sense been inverted, and hence the name.

CONSTITUTION OF THE SUGARS

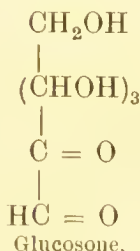
Much light has been thrown on the constitution of the sugars by the researches of Emil Fischer, which can only be very briefly referred to here. We now know that many sugars, besides glucose, have an aldehydic structure. These are called *aldoses*. Sugars which, like lævulose, are ketonic in structure, are now called *ketoses*. Our extended knowledge is largely due to the discovery that the various sugars form characteristic crystalline products with phenylhydrazine

$\left(\begin{array}{c} \text{NH}_2 \\ \text{NHC}_6\text{H}_5 \end{array} \right)$ (a body prepared from anilin by the action of sodium nitrite, and subsequent reduction by stannous chloride), which are more or less insoluble, and can be identified by their crystalline form and melting-point, so that the various sugars can be thus isolated and purified. For instance, glucose, if present, can be separated from urine by warming 50 c.c. with 1 grm. of phenylhydrazine hydrochloride and 2 grm. of sodium acetate. On allowing the mixture to cool, characteristic yellow needles

will separate. These crystals consist of a complicated compound called an *osazone*—in this case glucosazone.



Hydrochloric acid converts this into an osone, glucosone.



Nascent hydrogen reduces glucosone to lævulose, which can thus be obtained from glucose.

GLUCOSIDES

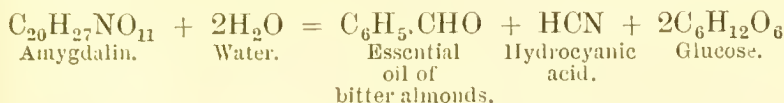
These may be defined as organic compounds which, when hydrolysed, yield glucose (or some other sugar) together with some other product *which is not a carbohydrate*. This hydrolysis may be effected (1) by boiling the glucoside with dilute acids or dilute alkalis; (2) by the action of a ferment often present in the plant to which the corresponding glucoside belongs.

Glucosides are generally crystalline solids, soluble in water; the following are examples:—

AMYGDALIN ($\text{C}_{20}\text{H}_{27}\text{NO}_{11}$)

This is a white crystalline substance present in bitter almond seeds, cherry-laurel leaves, and the

kernels of peaches, cherries, etc. Amygdalin is resolved, by boiling with dilute sulphuric acid, into essential oil of bitter almonds (benzoic aldehyde), hydrocyanic acid, and glucose. The same change is also produced by the action of a ferment named *emulsin* or *synaptase*, which is present, together with amygdalin, in almond seeds, cherry-laurel leaves, and the kernels of peaches, cherries, etc. This ferment is unable to act upon the amygdalin unless dissolved in water.



CATHARTIC ACID

This very complex glucoside exists in senna leaves, of which it is the active purgative principle; it is decomposed by boiling with dilute sulphuric acid into glucose and a substance named cathartogenic acid.

COLOCYNTHIN ($\text{C}_{56}\text{H}_{84}\text{O}_{23}$) (?)

This substance is the active purgative principle of colocynth pulp; it is decomposed by boiling with dilute sulphuric acid into glucose and a resinous substance.

DIGITALIN ($\text{C}_{27}\text{H}_{45}\text{O}_{15}$) (?)

This glucoside is the active principle of digitalis leaves; by boiling with dilute sulphuric acid, it is decomposed into glucose and a substance named digitaliretin.

INDICAN ($\text{C}_{26}\text{H}_{31}\text{NO}_{17}$) (?)

Occurs in the *Indigofera*, in woad and other plants; it is obtained as a yellowish bitter syrup. By boiling with dilute acids it is decomposed into indigo and a sugar (indigluin). The name has also been

erroneously applied to the substance, present in the urine, which produces indigo blue on standing; is not a glucoside, but is potassium indoxyl sulphate $[K(C_8H_6N)SO_4]$. The presence of this substance in the urine may be proved as follows: To about 20 c.c. of the sample, acidulated with an equal volume of strong HCl, add one or two drops of fresh solution of bleaching powder and then a little chloroform; mix well, and allow to stand. The chloroform soon acquires a blue tint (indigo).

JALAPIN ($C_{34}H_{56}O_{16}$)

This substance is the active purgative principle of jalap root; it is decomposed, by boiling with dilute sulphuric acid, into glucose and jalapinol.

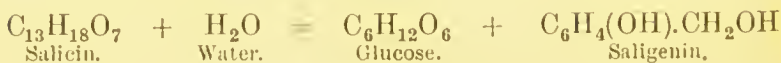
MYRONIC ACID ($C_{10}H_{19}NS_2O_{10}$)

This acid exists as a potassium salt in black mustard seeds; the salt is decomposed, by boiling with dilute sulphuric acid, and also by the action of a ferment *myrosin*, likewise contained in black mustard seeds, into volatile oil of mustard (allyl sulphocyanate), glucose, and potassium acid sulphate.



SALICIN ($C_{13}H_{18}O_7$)

This is a crystalline bitter principle contained in the leaves and bark of the willow; it is resolved by boiling with dilute sulphuric acid into glucose and an alcohol named saligenin.

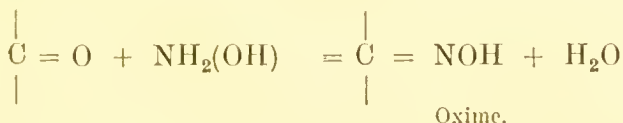


Addition of strong sulphuric acid to the solid salicin produces a crimson colour.

CHAPTER VII

ALDEHYDES AND KETONES

IN addition to what has already been said in connection with aldehyde and acetone, there are other features of these types to which brief reference must be made. Both contain the carbonyl group ($C=O$), and the reactions affecting this group are usually common to the two classes of compounds. Thus ketones, as well as aldehydes, show the reactions 2 and 3 (pages 461, 462); and the osazone reaction (page 487) is common to aldoses and ketoses. Both types react in the same way with hydroxylamine, $NH_2(OH)$, thus:



the compounds being distinguished as *aldoximes* and *ketoximes*.

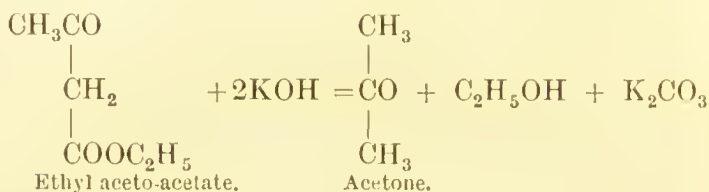
In the ketones the carbonyl group is always attached to *two* hydrocarbon radicles; in the aldehydes, to *one* radicle and a hydrogen atom.

Ketones are not so easily oxidised, and hence do not reduce ammoniacal silver nitrate solutions.

The preparations from barium and calcium salts (pages 456, 460) admit of general application. If, instead of the acetate, higher homologues of the salt are employed, then higher aldehydes and ketones will be obtained.

Another important general method for the pre-

paration of ketones is connected with the ethyl ester of aceto-acetic acid (page 471). If this is acted on by *dilute* potash, acetone is formed, thus :



The hydrogen in the CH_2 group of the ester may be replaced by CH_3 or higher radicles, and thus higher ketones be obtained in the same way.

CHAPTER VIII

ORGANIC ACIDS

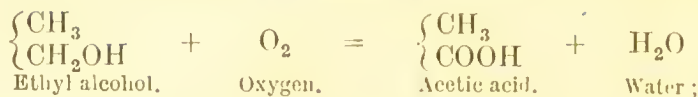
The Fatty Series—Monobasic Acids: Formic Acid—Acetic Acid—Propionic Acid—Lactic Acid—Butyric Acid— β Hydroxybutyric Acid—Palmitic, Stearic, and Oleic Acids—Fats—Saponification. Dibasic Acids: Oxalic Acid—Succinic, Malic, and Tartaric Acids. Tribasic Acids: Citric Acid.

ALL the organic acids which need be considered here, except prussic acid and uric acid, contain at least one carboxyl group (page 418). The basicity of any such acid depends upon the number of carboxyl groups contained in the molecule; formic acid is therefore monobasic, oxalic acid dibasic, etc. There are several homologous series of these acids, but the most important is the *fatty series*, so called because the higher members of the series are found as salts of glyceryl in fats. Many of these fatty acids are found in nature; thus, formic acid occurs in ants, butyric acid in rancid butter, etc.

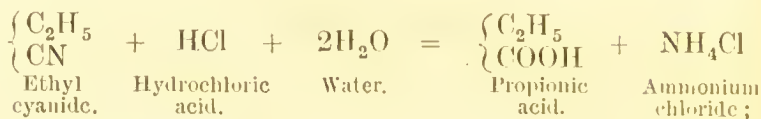
The fatty acids.—The general formula of this homologous series is $\begin{cases} \text{C}_n\text{H}_{2n+1} \\ \text{COOH} \end{cases}$. The first nine acids are colourless liquids, showing an average rise of about 22° in their boiling-points for each addition of CH_2 ; thus, acetic acid boils at 118° , propionic acid at 141° , and normal butyric acid at 162° .

The acid $\begin{cases} \text{C}_9\text{H}_{19} \\ \text{COOH} \end{cases}$ and higher members are solids.

These acids can be obtained (1) by oxidation of the corresponding alcohols or aldehydes (page 425)—

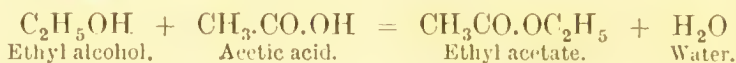


(2) by the action of bases or acids upon the corresponding nitriles (pages 430, 431)—



(3) by fermentation and destructive distillation of wood, etc.

General reactions.—1. Under suitable conditions the acid combines with the alcohol to form an *ester* (page 395).



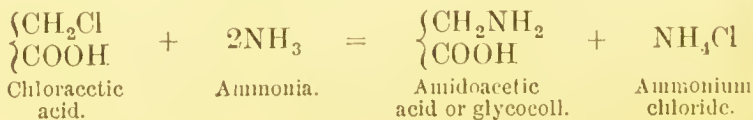
The bouquet in old wine is believed to be developed in this way owing to the slow formation of the fragrant esters.

2. Chlorine (or bromine) can replace the hydrogen in the radicle, as in a paraffin.

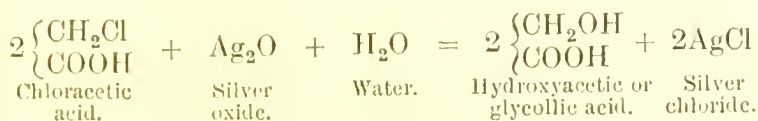


From these chloracids two other important series of derived acids are obtained :

(a) Heated with a solution of ammonia in alcohol the chlorine is replaced by the amidogen group, NH_2 , and an *amino-acid* is formed. Some of these are referred to later (page 533).

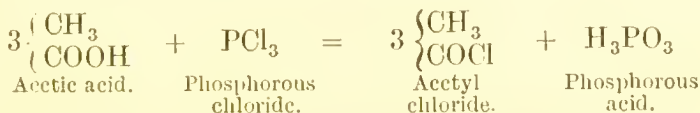


(b) When treated with moist silver oxide, the chlorine is replaced by hydroxyl, and a *hydroxyacid* is formed.

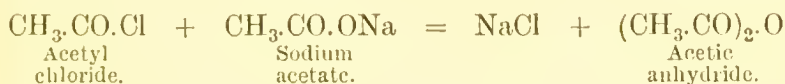


Lactic acid is an important member of this class, and is described later (page 500).

(3) If, instead of chlorine, we use phosphorous trichloride, the chlorine replaces the OH in the carboxyl group, the acid character of the body is lost, and we obtain the chloride of the acid radicle—e.g. acetyl chloride.



If the acid chloride be heated with the dry sodium salt of the acid, the corresponding anhydride is obtained; thus—

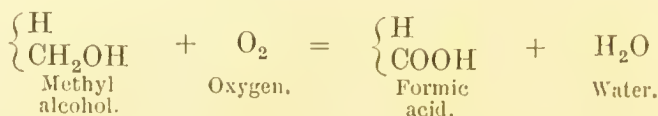


I. MONOBASIC ORGANIC ACIDS



This acid occurs in nature in red ants and in stinging-nettles. It can be prepared by the oxidation of methyl alcohol, either by dropping it on to spongy platinum, the occluded oxygen of which oxidises it to formic acid; or by distilling methyl alcohol with potassium bichromate and sulphuric

acid, which in presence of the alcohol evolve oxygen, with formation of potassium and chromium sulphates (see page 103).



Formic acid can also be prepared from sugar by oxidation with sulphuric acid and black oxide of manganese; but the best method is to heat crystallised oxalic acid with about twice its weight of glycerine in a flask or retort provided with a thermometer and connected to a condenser. The temperature should be kept within a few degrees of 105° ; a liquid containing about 50 per cent. of formic acid distils over. The glycerine remains unaltered, and may be used again with a fresh charge of oxalic acid.



If the proportion of glycerine be doubled, and also the temperature, allyl alcohol distils over instead.

Properties.—A clear, colourless liquid, of specific gravity 1.22, with a very penetrating odour; boils at 101° ; in its concentrated state it produces a blister when painted or rubbed on the skin. The wheals produced on the skin by the sting of the stinging-nettle are due to the injection beneath the skin of small quantities of formic acid when the hair of the stinging glands penetrates the skin.

Test.—1. An ammoniacal solution of silver nitrate is reduced to the metallic state on warming with formic acid, the silver forming a mirror-like deposit on the sides of the test-tube.

2. A solution of mercuric chloride is reduced to

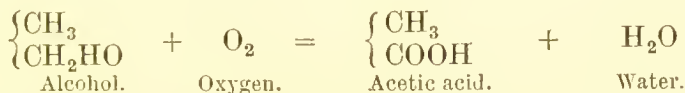
ealomel (precipitated), when *warmcd* with formic acid.

3. See page 499, test 3.



There are two prinicipal methods by which aetie acid is made: 1, the oxidation of alcohol; 2, the dry or destructive distillation of wood. *Vinegar* is obtained by the former proecess; *pyroligncous acid*, or crude aetie acid, by the latter.

1. **Brown or malt vinegar** is prepared by exposing beer, mixed with a little yeast, to the air; under the influence of a ferment, *Mycoderma aceti*, the aleohol of the beer becomes oxidised to acetic acid.



The vinegar so prepared contains about $5\frac{1}{2}$ per cent. of acetic acid; a small quantity of sulphuric acid is added at the last to destroy the ferment, and so prevent any further ehanges from taking plaee in the vinegar. It is to this development of acetic acid that the souring of beer is due when exposed to the air.

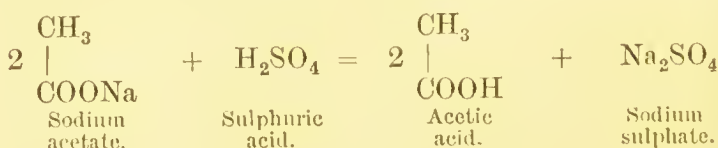
White-wine vinegar is prepared by the oxidation of the alcohol contained in the light white wines; the oxidation is facilitated by allowing the wine to trickle over the surface of wood-shavings contained in towers; in this way the alcohol of the wine becomes freely exposed to the action of the oxygen of the air, and so is rapidly converted into aetie acid.

Acetic acid may also be obtained by distilling the dry sodium salt with strong sulphuric acid (page 498).

2. Dry or destructive distillation of wood.

—Although wood contains no acetic acid, yet it contains the elements necessary for the formation of that body, and under the influence of dry heat, without exposure to air, a rearrangement of the elements of the wood takes place with the formation of several fresh bodies, amongst which is acetic acid. This process is the dry or destructive distillation of wood, and if the products are collected in different portions, as they distil over, a rough separation of them is effected, since the bodies with low boiling-points will distil before those with higher boiling-points. After the evolution of gaseous products (*wood gas*), the first portion of the distillate from the destructive distillation of wood consists of impure methyl alcohol, or *wood spirit*; next comes over impure acetic acid, or *pyroligneous acid*; *creosote* and other bodies distil over afterwards; and lastly *wood tar*, while *wood charcoal* remains in the retort.

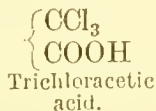
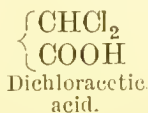
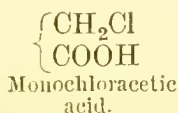
To obtain pure acetic acid from the pyroligneous acid, the latter is neutralised with sodium carbonate to form sodium acetate; the solution is then concentrated by evaporation, and, on cooling, crystals of sodium acetate separate out, leaving tarry and other impurities in the mother liquor. The crystals of sodium acetate are carefully heated, so as to expel any tar carried down with them, and the sodium acetate distilled with sulphuric acid, when pure acetic acid will be obtained as a distillate.



Properties of acetic acid.—Acetic acid, as usually seen, is a clear, colourless liquid, with a pene-

trating, pleasant acid odour, and an acid taste. The pure acid applied to the skin produces a blister. Ordinary acetic acid (*acidum aceticum*) is a mixture of acetic acid and water, containing about 33 per cent. of real acid. Glacial acetic acid (*acidum aceticum glaciale*) is pure acetic acid, and solidifies to a crystalline mass at temperatures below 15.5° ; it boils at 118° .

Three derivatives of acetic acid (chloracetic acids) are obtained by the action of chlorine on acetic acid, 1, 2, or 3 atoms of hydrogen being displaced from the acetic acid molecule, according to the amount of chlorine used. The acids are respectively called monochloracetic acid, dichloracetic acid, and trichloracetic acid.



Tests for acetic acid and acetates.—1. If an acetate is warmed with sulphuric acid, the odour of acetic acid is evolved.

2. If an acetate is warmed with sulphuric acid and alcohol, the sweet smell of ethyl acetate (acetic ether) is obtained.

3. If ferric chloride is added to a neutral solution of an acetate (or formate), a blood-red colour is produced, due to the formation of the soluble ferric salt; the colour is discharged by the addition of dilute hydrochloric acid. If the red neutral solution be boiled for some time, a dull red precipitate of the basic ferric salt is formed, the supernatant liquid becoming nearly colourless.

4. If a dry acetate be heated in a test-tube, the characteristic odour of acetone is evolved (see page 456).

5. Ammonium acetate when heated with phos-

phorus pentoxide yields water and acetonitrile (*see* page 430).

PROPIONIC ACID ($\text{CH}_3\cdot\text{CH}_2\cdot\text{COOH}$)

In this acid the radicle is composed of *two* hydrocarbon groups, and we have accordingly *two* varieties of each acid derived from it. When substitution takes place in the CH_2 group we obtain an α (alpha) acid; when in the CH_3 group, a β (beta) acid. Thus *α hydroxy-propionic acid* is $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{COOH}$, and is really lactic acid (page 421); but *β hydroxy-propionic acid* is $\text{CH}_2(\text{OH})\text{CH}_2\text{CO}\cdot\text{OH}$. The β acid has no asymmetric carbon atom, is optically inactive, and does not exhibit the stereo isomerism which is such an interesting feature of the α acid. We have already (page 421) distinguished the three varieties of this important acid, but must now refer in fuller detail to the ordinary acid.

Preparation of ordinary or fermentation lactic acid.—This acid is best obtained by the process known as the *lactic acid fermentation* of sugar, which is effected by the action of the ferment, *Penicillium glaucum*, on either glucose or milk sugar. Under the influence of this ferment, both these sugars split up into lactic acid; the glucose molecule becoming resolved into two molecules of lactic acid, thus:



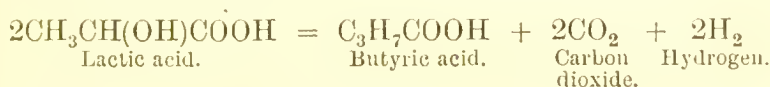
the milk-sugar molecule is resolved into four molecules of lactic acid—



The production of lactic acid by fermentation is best effected by taking a mixture of sugar, mouldy

cheese (the mould of which is *Penicillium glaucum*), chalk, and water, and leaving the mixture for some time in a warm place; the lactic acid as it is formed is converted by the chalk into calcium lactate, which is deposited as a crystalline mass. From the calcium lactate the lactic acid may be set free by the addition of sulphuric or oxalic acid; on filtering from the insoluble calcium sulphate or oxalate, and evaporating the filtrate, the lactic acid is obtained as a syrupy liquid.

If the fermentation is allowed to continue too long, then the lactic acid becomes decomposed by a further fermentative process into butyric acid (*see* page 502), thus :



The presence of lactic and butyric acids in the stomach is a symptom to which considerable importance is sometimes attached.

Lactic acid may be obtained from aldehyde by (1) formation of the cyanhydrin (*see* page 462); (2) conversion of the CN group in this to COOH by hydrochloric acid (*see* page 430). This cyanhydrin may, in fact, be regarded as the nitrile of lactic acid; the constitution of this acid is thus clearly established.

When distilled with dilute sulphuric acid, lactic acid accordingly yields aldehyde and formic acid. When distilled with dilute sulphuric acid and manganese peroxide, the formic acid is oxidised, and we obtain aldehyde and carbonic anhydride.

Ordinary lactic acid has no action on polarised light, and its zinc salt crystallises with three molecules of water [$\text{Zn}(\text{C}_3\text{H}_5\text{O}_3)_2 + 3\text{H}_2\text{O}$]; 1 part of the salt requires 58 parts of water for its solution.

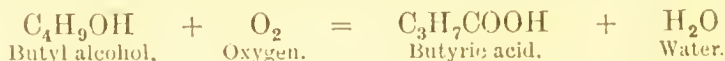
The isomer obtained from flesh (*sarcolactic acid*)

is dextrorotatory. Its zinc salt has the formula $\text{Zn}(\text{C}_3\text{H}_5\text{O}_3)_2 + 2\text{H}_2\text{O}$, and 1 part of the salt dissolves in 17 of water.

The souring of milk on exposure to the air is due to the conversion of the milk sugar into lactic acid, the fermentation being induced by the spores of *Penicillium glaucum*, which are always present in the air, settling on the surface of the exposed milk.

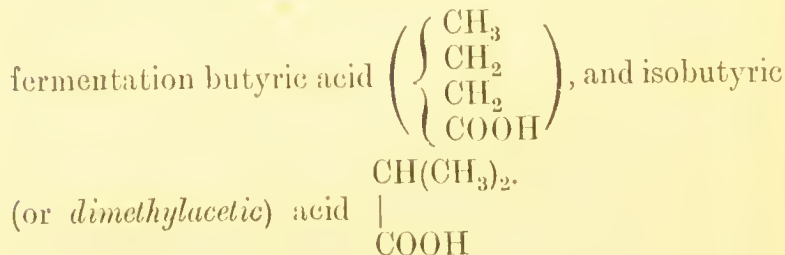


This acid is contained in human perspiration, and in rancid butter. It is prepared, as a rancid-smelling oily fluid, by the oxidation of butyl alcohol with potassium bichromate and sulphuric acid.



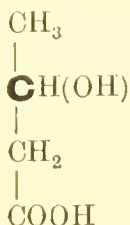
Butyric acid can also be obtained from lactic acid by a fermentation process (*see* page 501).

Two varieties of butyric acid exist, normal or

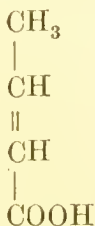


β HYDROXY-BUTYRIC ACID

This acid is of clinical interest; its presence in the urine of diabetic patients is a symptom to which considerable importance is attached. The formula of the acid is—



One of the carbon atoms, shown in heavy type, is asymmetric; the acid found in urine is lævoptatory. An inactive variety can be obtained by the reduction of acetoacetic acid (page 471), to which it is closely related. Another near relative is acetone (page 456), with which it is also often associated. When distilled with sulphuric acid, the β acid loses the elements of a molecule of water and becomes converted to crotonic acid—

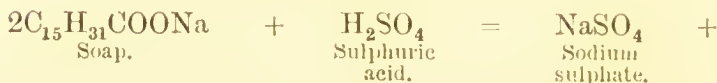
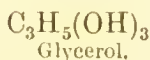


The estimation of it in urine is based upon this reaction.

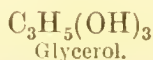


This acid is found in spermaceti, beeswax, palm oil, etc. It is prepared by saponifying palm oil by boiling with caustic soda, when a soap, sodium palmitate, is formed, together with glycerol; the soap is separated by throwing in salt, and finally, on decomposing the soap by boiling with dilute sulphuric acid, sodium sulphate and palmitic acid are formed.

The equations representing the above reactions are as follows :—



A second plan is to decompose a natural fat containing the acid with superheated steam, when the free fatty acid and glycerol are formed.



Palmitic acid is a white crystalline solid, insoluble in water, soluble in boiling alcohol and in ether. Melts at 62°.



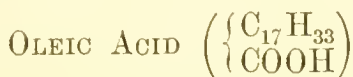
This acid does not seem to occur in natural fats, but can be prepared synthetically.



Occurs in beef-suet, mutton-suet, cacao butter. It is prepared from these fats by processes similar to those described under Palmitic Acid. Stearic acid closely

resembles palmitic acid, but melts at 69° . Both acids are extensively used for the manufacture of candles.

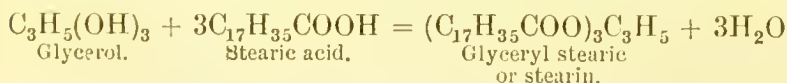
A third acid, which is a liquid, is commonly found associated with palmitic and stearic acids in the natural fats :



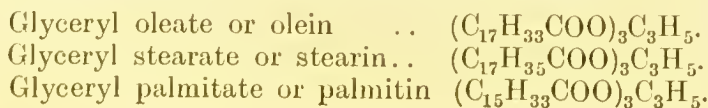
This is not, strictly speaking, a member of the fatty, or acetic, series of acids. It is unsaturated, and belongs really to a different series—the acrylic series. It occurs in olive and almond oil. When pure, it solidifies in white crystals at 14° . It is insoluble in water and easily soluble in alcohol.

FATS AND FIXED OILS

A fat or oil is a compound of the radicle glyceryl with the acid radicle of one of the higher fatty acids. The large majority of fats and oils consist of the radicle glyceryl united with the oleic, stearic, and palmitic radicles. The compound of glyceryl and the oleic radicle is glyceryl oleate, or *olein* ; the compound of glyceryl and the stearic radicle is glyceryl stearate, or *stearin* ; and the compound of glyceryl and the palmitic radicle is glyceryl palmitate, or *palmitin*. These are normal salts, formed by the reaction of one molecule of the trivalent base glycerol with three molecules of one of these monobasic acids—e.g.



The formulæ of these fats and oils are, therefore, as follows :—



Olein is a liquid, stearin and palmitin are solids; therefore the larger the proportion of olein in a mixed fat the softer it will be; and the larger the proportion of stearin (which is harder than palmitin) the harder the mixed fat will be.

Olein is the chief constituent of olive oil and almond oil, and is also contained in eastor oil. *Stearin* forms the bulk of beef-suet and mutton-suet. *Palmitin* is present in palm oil. Human fat is a mixture of olein, stearin, and palmitin. *Margarine*, which was formerly believed to be a simple fat, is now known to be a mixture of stearin and palmitin.

Olive oil is a type of the non-drying oils—i.e. oils which, when exposed to the air, become thick and acid, but do not harden. Linseed, poppy, and hemp oils, which are glycerides of linoleic acid, dry up to a hard varnish, and are termed drying oils.

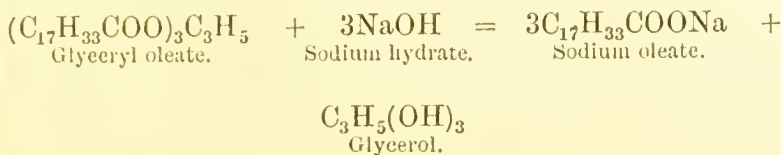
SOAPS AND SAPONIFICATION

A soap is a compound of a metal with the radicle of oleic, stearic, or palmitic acid, and is therefore obtained by the displacement of the glyceryl of an oil or fat by a metal. The following list shows the chief constituents of the commonly used soaps:—

Common, yellow, or hard soap }	
consists of <i>sodium oleate</i> , &c. }	$C_{17}H_{33}COONa$
Soft soap consists of <i>potassium</i>	
<i>oleate</i> , &c. 	$C_{17}H_{33}COOK$
Curd soap consists of <i>sodium</i>	
<i>stearate</i> , &c. 	$C_{17}H_{35}COONa$

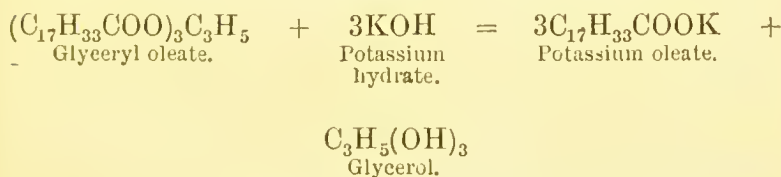
Saponification is the process by which oils or fats are converted into soaps, and consists in decomposing the oil or fat with an alkali, when double decomposition takes place, resulting in the formation of a soap and glycerol.

Hard Soap.—This is prepared by boiling olive oil, cocoanut oil, suet, etc., with caustic soda, when double decomposition occurs, as follows :—



When the process of saponification is completed, common salt is added to separate the soap from the glycerol; the soap, being insoluble in a solution of common salt, is thrown out of solution on the addition of the salt, and rises to the surface of the liquid, when it can be removed.

Soft Soap.—This is prepared by boiling olive oil and other fats with caustic potash, when double decomposition occurs, as follows :—



Common salt cannot be used to throw this soap out of solution, as it would convert it into the soda soap; the solution is therefore evaporated to a soft consistence, the glycerol being left in the soap.

The term saponification, originally applied to the decomposition of the fats by boiling with a caustic alkali, by which a soap was formed, is now extended to the similar decomposition of any ester, e.g. ethyl acetate (*see* page 470), even though the alkali salt produced is not, in the technical sense of the word, a soap. Chemically, the reactions are the same; an ester is decomposed by a caustic alkali with forma-

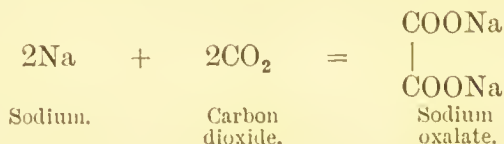
tion of the alkali salt of the organic acid and separation of the alcohol.

II. DIBASIC ORGANIC ACIDS

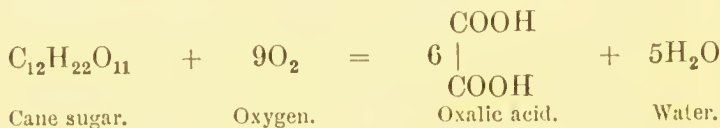
OXALIC ACID $\left(\begin{matrix} \text{COOH} \\ \text{COOH} \end{matrix} \right)$

This acid is present in the form of potassium and calcium salts in a few plants, such as the wood-sorrel, rhubarb, and common dock. There is not, however, a sufficient quantity of it in these plants to render its extraction from them a commercial success, and it is therefore obtained by an artificial process. It may be prepared—

1. In the form of its sodium salt by passing carbon dioxide over carefully heated metallic sodium.

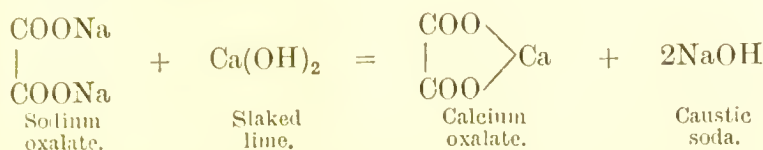


2. It may also be prepared by boiling cane sugar with strong nitric acid, some of the oxygen of which oxidises the sugar to oxalic acid.

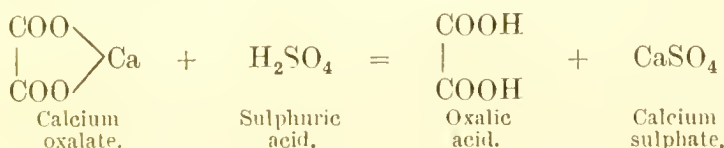


3. On the manufacturing scale, oxalic acid is prepared from sawdust. The process is carried out on a large scale by heating sawdust to a temperature of 204° with caustic soda on iron plates, care being taken not to use sufficient heat to char the sawdust; the sodium oxalate is then extracted by means of boiling water, and decomposed by slaked lime into

the insoluble calcium oxalate and caustic soda; the latter can then be used for heating with a fresh portion of sawdust.



The calcium oxalate is then decomposed with sulphuric acid and water, with formation of insoluble calcium sulphate and soluble oxalic acid; on filtering from the calcium sulphate, and concentrating the filtrate by evaporation, crystals of oxalic acid are deposited.



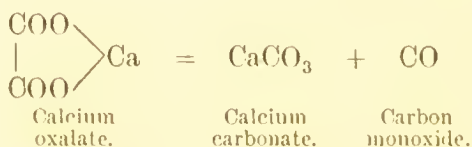
Properties $\left(\begin{array}{c} \text{COOH} \\ | \\ \text{COOH.2H}_2\text{O} \end{array} \right)$.—Oxalic acid is a

white crystalline solid, with a very acid taste; it is an irritant poison, the antidote for it being chalk or lime-water, either of which neutralises the oxalic acid, and forms the insoluble calcium oxalate; on gently heating it, water is evolved, and the anhydrous acid $(\text{COOH})_2$ sublimes. When treated with PCl_5 the OH groups are not replaced by Cl, but the acid is decomposed with formation of the two oxides of carbon, HCl, and POCl_3 .

Salt of sorrel $\left(\begin{array}{c} \text{COOH,} \\ | \\ \text{COOK,} \end{array} (\text{COOH})_2\text{H}_2\text{O} \right)$ is an acid

potassium oxalate combined with oxalic acid; it exists in the wood sorrel, and may be made by one-

fourth neutralising oxalic acid with potassium carbonate; salt of sorrel and oxalic acid are both used for removing ink-stains from linen, the tannate of iron of the ink-stain being soluble in a solution of oxalic acid. Heat decomposes oxalic acid into water and the two oxides of carbon; a similar decomposition, but at a lower temperature, takes place when oxalic acid is heated with strong sulphuric acid (*see* page 201). Oxalates of the metals when heated yield carbonates, with evolution of carbon monoxide, thus:



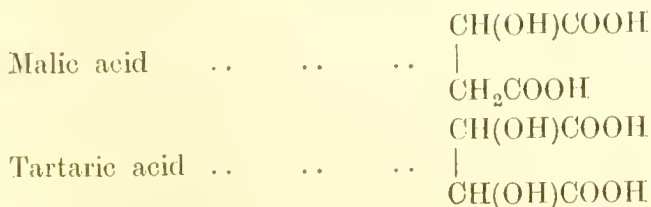
Tests for oxalic acid.—1. If a solution of oxalic acid be neutralised with ammonia, and calcium chloride be added, a white precipitate of calcium oxalate will be thrown down; this precipitate is insoluble in acetic acid, but is soluble in hydrochloric acid.

2. When boiled with strong sulphuric acid, oxalic acid and the oxalates evolve CO and CO₂, but do not char; if MnO₂ be added, only CO₂ is obtained.

SUCCINIC ACID

This acid can be obtained from amber by heat: hence its name (from *succinum*, amber). Although not employed at all in medicine, it is of interest on account of its relationship to malic and tartaric acids, as will be seen from the following formulæ:—





Malic acid is therefore hydroxysuccinic acid, and tartaric is dihydroxysuccinic or hydroxymalic acid. Succinic acid is formed in small quantities in the alcoholic fermentation. It crystallises in colourless prisms, melting at 180° ; it readily sublimes.

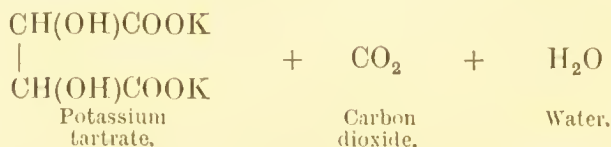
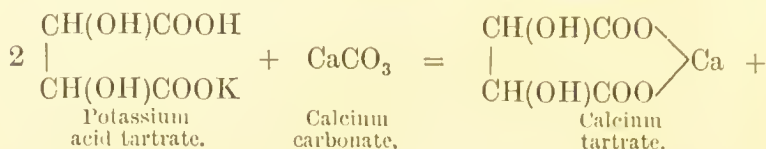
MALIC ACID

This acid is present in the free state in apples, pears, cherries, berries of the mountain ash, and various other fruits; it is also present in considerable quantities in green garden rhubarb, the sourness of which is due to malic acid. It is not used in medicine, but is of interest as being intermediate in composition between succinic and tartaric acids (*see above*).

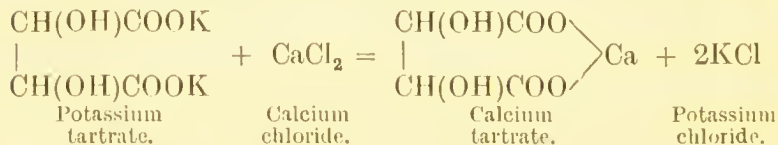
TARTARIC ACID

This acid occurs as potassium acid tartrate (cream of tartar) in grapes, tamarinds, pine-apples, and several other fruits. It is deposited as *argol* during the fermentation of grape juice; for, although the potassium acid tartrate is soluble in the grape juice, it is insoluble in alcohol, and is therefore precipitated as the grape sugar becomes converted into alcohol. Argol consists of potassium acid tartrate coloured with some of the colouring matter of the wine; it also constitutes the *crust*, formed as a sediment, in old port and other wines. *Cream of tartar*, or *bitartrate of potash*, as it is sometimes called, is argol deprived of its colouring matter by means of animal charcoal and recrystallisation.

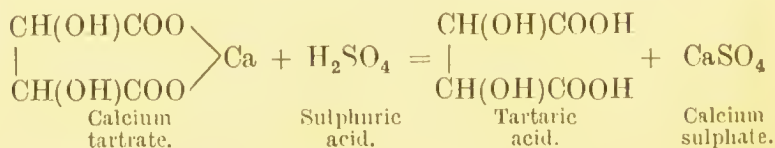
Preparation.—Tartaric acid is prepared by dissolving cream of tartar in boiling water, and adding chalk till effervescence ceases, when one-half of the tartaric radicle is precipitated as calcium tartrate, the other half remaining in solution as potassium tartrate.



Calcium chloride is then added to decompose the potassium tartrate, so that the whole of the cream of tartar is converted into the insoluble calcium tartrate.



The calcium tartrate is finally decomposed with sulphuric acid and water, with the production of insoluble calcium sulphate and soluble tartaric acid; on filtering from the calcium sulphate, and concentrating the filtrate by evaporation, crystals of tartaric acid are deposited.



Properties.—Tartaric acid is a white crystalline solid, with a very acid taste. The molecule of tar-

tartic acid contains two asymmetric carbon atoms; they are printed in heavy type in the graphical formulæ on this page. Four varieties of tartaric acid are known; two of these are optically active, viz.—

1. Ordinary, or dextro-, tartaric acid (I.).

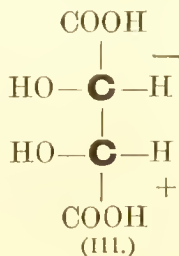
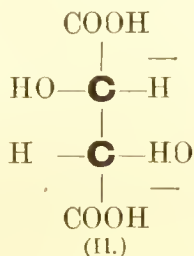
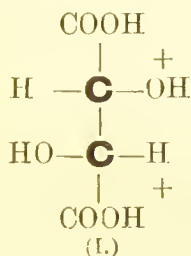
2. Lævo-tartaric acid (II.).

The other two are optically inactive, viz.—

3. Racemic acid.

4. Mesotartaric acid (III.).

A solution of 3 is inactive because it contains an equal number of molecules of 1 and 2, but each individual molecule is active. A solution of 4 is inactive because each individual molecule is inactive.



If the groups be arranged as in I., the two halves of the molecule will have a similar structure; i.e. looking at the two asymmetric carbon atoms from each end, it will be seen that the hydrogen atom is on the right of each carbon atom. Let us suppose this to be the *dextrotartaric* acid and mark it by a +. Two other modifications are possible, II. and III. Formula II. is the reverse of I., and the hydrogen atoms are on the left of the carbon atoms, and this will be the constitution of the *lævotartaric* acid. Racemic acid is a *mechanical* mixture of dextro- and lævotartaric acids, I. and II., and can be separated mechanically by picking out the two forms of crystals with a magnifying glass, having first converted the racemic acid into the sodium ammonium racemate

(*see also* page 423). Finally the mesotartaric molecule (III.) has the lower half of I. with the upper half of (II.), and is therefore inactive by internal compensation.

Tests.—1. If to a solution of tartaric acid carefully neutralised with ammonia some silver nitrate be added, a white precipitate of silver tartrate is thrown down; on heating the mixture, a precipitate of metallic silver forms as a mirror-like deposit on the sides of the test-tube.

2. When shaken with a solution of calcium chloride neutral solutions of tartrates give a white precipitate.

3. When heated with strong sulphuric acid, a tartrate chars, evolves CO and CO₂, and acquires an odour of burnt sugar.

III. TRIBASIC ORGANIC ACIDS



This acid is present in lemons, limes, currants, gooseberries, raspberries, etc. It is prepared from lemon-juice or lime-juice by first boiling the juice and filtering from any suspended matters, and then adding chalk until effervescence ceases; the precipitated calcium citrate is collected and decomposed with sulphuric acid in a manner similar to that employed in the preparation of tartaric acid.

Properties and tests.—Citric acid is a white crystalline solid, with a very acid taste. The solid, when heated with strong sulphuric acid, first turns of a pale lemon colour, passing successively to a darker yellow colour, a sherry colour, a port-wine colour, and finally becoming black.

Citrates give no mirror with silver salts, and no precipitate with calcium chloride in the cold.

CHAPTER IX

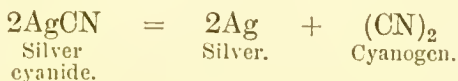
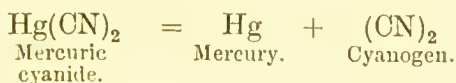
CYANOGEN GROUP

Cyanogen—Potassium Ferrocyanide—Potassium Cyanide—Hydrocyanic Acid—Tests for Hydrocyanic Acid and Cyanides—Potassium Ferricyanide—Methyl Cyanide—Ethyl Cyanide—Potassium Thiocyanate—Potassium Cyanate—Ammonium Cyanate—Urea—Uric Acid—Amino-Acids.

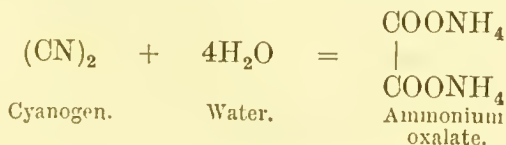
CYANOGEN (CN)₂

THE name cyanogen (from *κύανος*, blue; *γεννάω*, to generate) is due to the fact that some of the double cyanogen compounds possess brilliant blue colours.

Preparation. — Cyanogen is a gas, and is obtained by heating either mercuric cyanide or silver cyanide.



Properties. — Cyanogen is a colourless gas, possessing a peculiar odour somewhat resembling that of the essential oil of bitter almonds; it is soluble in water, and is very poisonous. The solution, on keeping, is converted into ammonium oxalate.



The same change takes place more rapidly in the presence of acids or alkalies. Cyanogen is therefore the *nitrile* (see page 431) of oxalic acid. It burns with a characteristic coloured flame, the colour resembling that of the peach blossom, and it produces carbon dioxide and free nitrogen when burnt. Its specific gravity is 26, and it is therefore much heavier than air; its molecular weight is 52, and its formula $(\text{CN})_2$. CN is often written Cy.

There are points of resemblance between cyanogen and chlorine. When cyanogen is passed into caustic potash, salts are obtained corresponding to the chloride and hypochlorite (see page 182), thus:

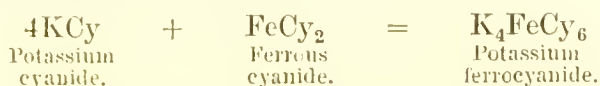


Test.—The odour of the gas, combined with the peculiar colour of its flame when burnt, constitutes the best means for the recognition of cyanogen.

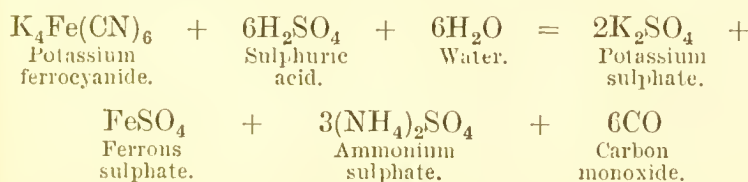
POTASSIUM FERROCYANIDE ($\text{K}_4\text{FeCy}_6\cdot 3\text{H}_2\text{O}$)

This body is the ancestor of the cyanogen compounds. Since no cyanogen compounds exist in nature, it is necessary that one or more of them should be made by some artificial process, and the cyanogen compound that is prepared artificially is potassium ferrocyanide. To prepare this substance it is necessary to employ some potassium salt to furnish the potassium, the metal iron to furnish the iron, and some organic substance, rich in carbon and nitrogen, to furnish the elements for the production of the cyanogen. It is made, therefore, by fusing together potassium carbonate, iron filings, and animal matter, such as hoofs, horns, and scraps of hide, substances that are rich in both carbon and nitrogen. Under

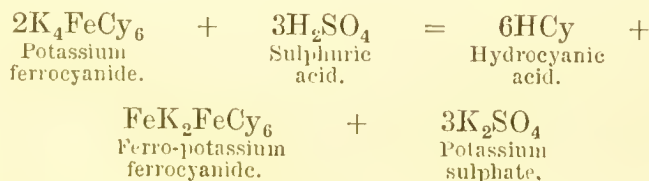
the influence of the heat, and in presence of the other substances, the carbon and nitrogen unite to form cyanogen, which, with the potassium carbonate, forms potassium cyanide (KCy), and with the iron forms ferrous cyanide (FeCy_2). On boiling the melted mass with water, these two cyanides unite to form potassium ferrocyanide.



Properties.—Potassium ferrocyanide occurs in yellow crystals, and is commonly known as *yellow prussiate of potash*. Although the powerful poisons hydrocyanic acid and potassium cyanide are made from it, yet potassium ferrocyanide itself is non-poisonous. It is decomposed when strongly heated, with production of potassium cyanide and carbide of iron. Potassium ferrocyanide is decomposed by both strong and dilute sulphuric acid, but with different results in the two cases. If heated with strong sulphuric acid, carbon monoxide is copiously evolved.



If heated with dilute sulphuric acid, hydrocyanic acid only is evolved.



Potassium ferrocyanide is used in the manufacture of *Prussian blue*, which is ferric ferrocyanide

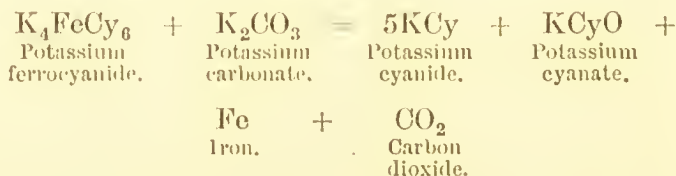
[$\text{Fe}_4(\text{FeCy}_6)_3$]. It is prepared by adding potassium ferrocyanide to a solution of ferrous sulphate, and oxidising the precipitate thus obtained with dilute nitric acid or chlorine water.

Tests.—1. Potassium ferrocyanide gives with a solution of ferric chloride a dark blue precipitate.

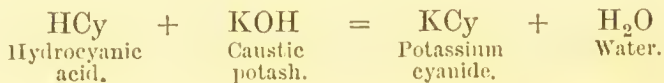
2. A solution of copper sulphate gives with potassium ferrocyanide a reddish-brown precipitate of copper ferrocyanide. This is a most delicate test for the salt.

POTASSIUM CYANIDE (KCy)

This salt is prepared in the form of commercial cyanide of potassium, used for electroplating, etc., and also as the pure cyanide of potassium. The commercial cyanide of potassium may be prepared by strongly heating potassium ferrocyanide alone (page 517), but it is most conveniently prepared, at a lower temperature, by fusing together potassium ferrocyanide and potassium carbonate. The cyanide of potassium prepared by this process is, however, always mixed with some cyanate.

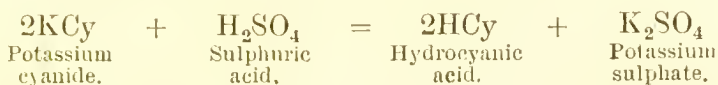


Pure cyanide of potassium may be prepared by neutralising hydrocyanic acid with caustic potash; this is most conveniently effected by passing the vapour of hydrocyanic acid into an alcoholic solution of caustic potash, when the potassium cyanide crystallises out as it is formed.

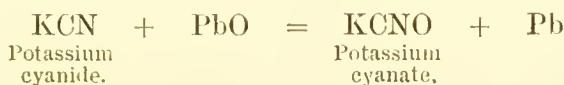


Potassium cyanide may also be prepared by utilising the nitrogen of the air; thus by passing air over a mixture of potassium carbonate and charcoal strongly heated, potassium cyanide is formed and carbon monoxide evolved.

Properties.—Potassium cyanide is a white crystalline solid, evolving, on exposure to the air, the odour of hydrocyanic acid. It is very poisonous, and is readily acted on by acids, hydrocyanic acid being evolved.



Potassium cyanide is a powerful reducing substance; thus when heated with litharge it forms metallic lead and potassium cyanate.



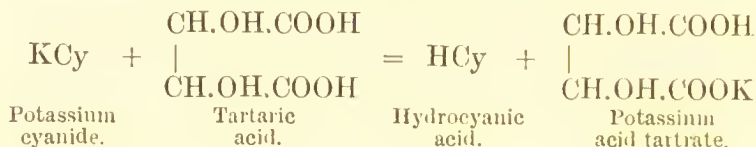
Aqueous solutions of potassium cyanide have an alkaline reaction, because they contain the free ions of caustic potash, namely, K and OH; while the weak, or slightly ionised, prussic acid (HCy) also exists in the solution and can be detected by its odour.

Tests.—The tests for potassium cyanide are the same as those for hydrocyanic acid (pages 523, 524).

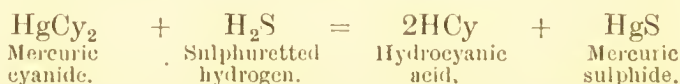
HYDROCYANIC ACID (HCN OR HCy)

This acid is commonly known as *prussic acid*, having been first prepared from Prussian blue; it may be prepared from potassium ferrocyanide or from any metallic cyanide. The hydrocyanic acid used in medicine (*acidum hydrocyanicum dilutum*) is prepared by distilling potassium ferrocyanide

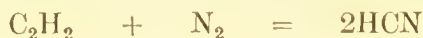
with dilute sulphuric acid (page 517), and diluting the distillate to the required strength. It may also be prepared by shaking together solutions of potassium cyanide and tartaric acid, when the potassium acid tartrate is deposited on standing, leaving the hydrocyanic acid in solution.



Pure hydrocyanic acid is seldom prepared on account of its extremely poisonous nature and the danger incurred by the operator in its preparation. It may be obtained by passing dried sulphuretted hydrogen gas over heated mercuric cyanide, the hydrocyanic acid vapour being condensed in a suitable apparatus surrounded by a freezing mixture.



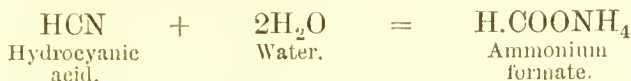
Hydrocyanic acid has also been formed by sparking a mixture of acetylene and nitrogen.



Hydrocyanic acid is present, possibly as a cyanhydrin, in the *essential oil of bitter almonds*, being produced from the decomposition of the glucoside amygdalin under the influence of the ferment emulsin present in the almonds, the presence of water being necessary for the emulsin to act on the amygdalin (page 489).

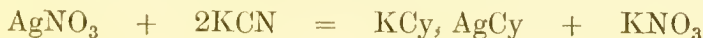
Properties.—The pure acid is a colourless, volatile liquid, which boils at 26° and freezes at -15° . It has a characteristic odour, suggestive of

bitter almonds, to which the back of the throat seems to be peculiarly sensitive. It does not redden litmus. It is an extremely powerful and rapidly acting poison; only a very dilute solution of it is employed in medicine, the Diluted Hydrocyanic Acid, B. P., being of only 2 per cent. strength. If dilute hydrocyanic acid be kept for some time with exposure to light it slowly decomposes, becoming converted into ammonium formate.



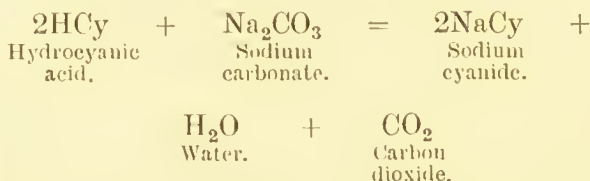
HCN can also be formed from ammonium formate by depriving it of two molecules of water, and is therefore sometimes called formonitrile; in the same way acetonitrile or methyl cyanide can be obtained by heating ammonium acetate with phosphoric anhydride (*see* page 430).

Hydrocyanic acid is contained not only in essential oil of bitter almonds but in essence of peach kernels, essence of cherry kernels, bitter-almond water and cherry-laurel water. The strength of hydrocyanic acid can be determined by ascertaining the weight of silver cyanide precipitated by adding an excess of silver nitrate solution to a known quantity of the diluted hydrocyanic acid. It is, however, usually estimated by a volumetric method which is based upon the fact that silver cyanide (AgCy) dissolves in solution of potassium cyanide owing to the formation of a double cyanide KCy, AgCy, which is, like most potassium compounds, soluble in water. Only when all the potassium cyanide in solution is thus employed will a permanent precipitate begin to appear. Its appearance will therefore indicate the completion of the following reaction:—

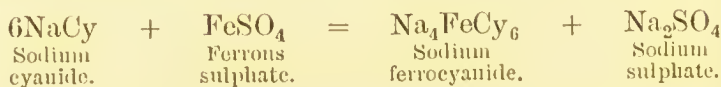


The method therefore consists in (1) making the solution of prussic acid alkaline by addition of caustic potash; (2) titrating a known volume of this alkaline solution with decinormal solution of silver nitrate delivered from a burette till a permanent precipitate *begins* to appear—1 c.c. of $\frac{N}{10}$ $\text{AgNO}_3 = \cdot 0054$ grm. of HCy .

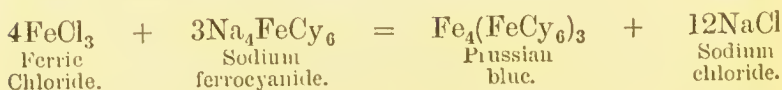
The antidote, in cases of poisoning by hydrocyanic acid, is to convert the soluble and diffusible hydrocyanic acid into the insoluble Prussian blue. This is effected by giving a draught containing a mixture of sodium carbonate, ferrous sulphate, and ferric chloride. The sodium carbonate forms sodium cyanide.



This, with the ferrous sulphate, forms sodium ferrocyanide.



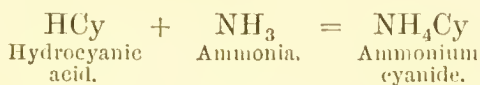
And this, with the ferric chloride, forms Prussian blue.



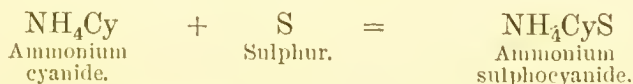
As a matter of fact, hydrocyanic acid is so rapid in its action as a poison, that, as a rule, there is not time to obtain and administer so complex an antidote as the one just described.

Tests.—1. *Prussian blue test.*—This consists in adding to the hydrocyanic acid, caustic soda, solution of ferrous sulphate, solution of ferric chloride, heating, and then acidifying with hydrochloric acid. The first three reagents act as described in connection with the antidote (page 522); the hydrochloric acid is finally added to neutralise any excess of caustic alkali, which would, if present, prevent the development of the Prussian blue.

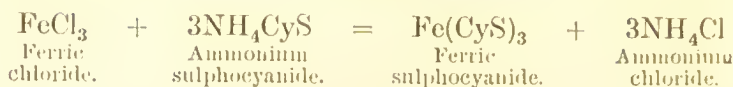
2. *Sulphocyanide test.*—This depends on the conversion of the hydrocyanic acid into ferric sulphocyanide, which is of a deep blood-red colour. This conversion is effected by adding to the hydrocyanic acid solution of ammonia and then a few drops of yellow ammonium sulphide, and evaporating the mixture to a low bulk on the water bath; to the concentrated liquid, hydrochloric acid and ferric chloride are then added, when the deep blood-red colour of ferric sulphocyanide is produced. The solution of ammonia converts the hydrocyanic acid into ammonium cyanide.



The free sulphur contained in the yellow ammonium sulphide then converts this ammonium cyanide into ammonium sulphocyanide.



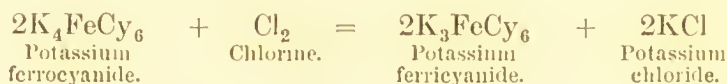
This sulphocyanide, on the addition of ferric chloride, forms the blood-red ferric sulphocyanide. The hydrochloric acid is merely added to decompose any excess of ammonium sulphide that may be present, which would otherwise cause the formation of black sulphide of iron.



3. The cyanides resemble the chlorides in giving with silver nitrate a white curdy precipitate, which is insoluble in dilute nitric acid, but soluble in ammonia solution. In the case of the cyanide, the precipitate is soluble in potassium cyanide.

POTASSIUM FERRICYANIDE (K_3FeCy_6)

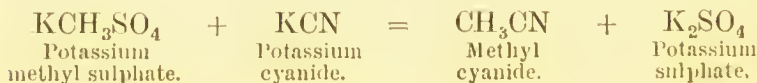
This is prepared from potassium ferrocyanide by increasing the valency of the iron from two to three, that is, by *oxidation*.



Properties.—Potassium ferricyanide occurs in reddish-brown crystals, and is commonly known as *red prussiate of potash*. With a solution of a ferrous salt potassium ferricyanide gives a dark blue precipitate. With ferric salts it gives no precipitate at all, but merely a dark olive-green colour, and hence it is readily distinguished from potassium ferrocyanide, which with ferric chloride gives a dark-blue precipitate. It is a powerful oxidising substance.

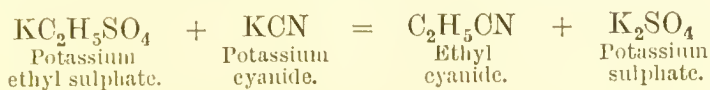
METHYL CYANIDE (CH_3CN)

This alcoholic cyanide is prepared by distilling the potassium salt of methyl sulphuric acid with potassium cyanide (*see also* page 430).

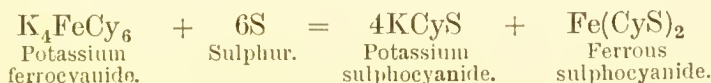


ETHYL CYANIDE (C_2H_5CN)

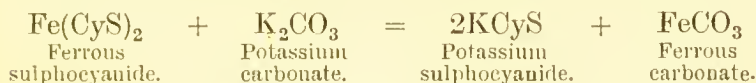
This is prepared in a similar manner to methyl cyanide by distilling the potassium salt of ethyl sulphuric acid with potassium cyanide.

POTASSIUM THIOCYANATE OR SULPHOCYANIDE
($KCNS$)

This may be prepared by fusing together potassium ferrocyanide and sulphur.



The fused mass is then boiled with water and potassium carbonate added to convert the ferrous sulphocyanide into potassium sulphocyanide and ferrous carbonate, the latter being precipitated.



The soluble sulphocyanides may also be prepared by direct union of the soluble cyanides and sulphur, as in the sulphocyanide test for hydrocyanic acid (*see* page 523). Potassium sulphocyanide is present in minute quantities in the saliva of man.

Test.—Potassium sulphocyanide gives with ferric chloride a deep blood-red colour. This colour is not discharged on the addition of dilute hydrochloric acid; it is thus distinguished from the blood-red colour given by ferric chloride with an acetate, the colour of ferric acetate being discharged by dilute

hydrochloric acid (*see* page 499). The colour of ferric sulphocyanide is discharged on the addition of a solution of mercuric chloride, and in this way it is distinguished from the blood-red colour given by ferric chloride with meconic acid or a meconate, since this is not discharged by mercuric chloride (*see* Chapter XI, Alkaloids).

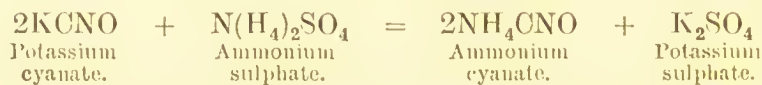
CYANATES AND UREA

POTASSIUM CYANATE (KCNO)

This may be prepared by exposing fused potassium cyanide for some time to the air, when oxygen is absorbed and the cyanate formed; or it may be prepared by dropping a metallic oxide, such as lead oxide, into the fused potassium cyanide; the latter unites with the oxygen of the lead oxide, forming potassium cyanate, and the metal lead is set free (*see* page 519).

AMMONIUM CYANATE (NH_4CNO)

This salt is prepared by mixing solutions of potassium cyanate and ammonium sulphate, when double decomposition takes place.



Alcohol is then added to precipitate the potassium sulphate, leaving the ammonium cyanate in solution. This salt is of interest as its isomer *urea* [$\text{CO}(\text{NH}_2)_2$] can be prepared from it. The conversion of ammonium cyanate into urea is effected by simply evaporating its solution to dryness on the water-bath, when urea is left; the temperature of boiling water is therefore sufficient to change ammonium cyanate into urea. The urea, in its turn, may be reconverted

into ammonium cyanate by raising it to a dull-red heat, when ammonia gas is evolved and cyanuric acid formed.



If the cyanuric acid be more strongly heated, it splits up into cyanic acid, which distils over.



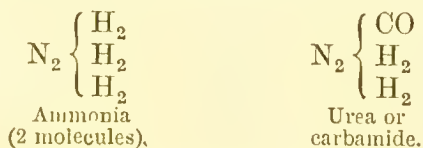
If the cyanic acid is neutralised with ammonia, ammonium cyanate is reproduced.

Two isomeric forms of the cyanates exist. The formula of ammonium cyanate is probably $(\text{NH}_4) \text{—O—C} \equiv \text{N}$, while ammonium isocyanate would be represented by the formula $(\text{NH}_4) \text{—N} = \text{C} = \text{O}$. Two corresponding forms of the thiocyanates probably exist.

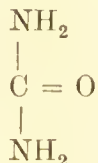
As urea is so closely connected with ammonium cyanate (or isocyanate), it will be convenient to consider it here, although it belongs to the amides (*see* page 427).

UREA, OR CARBAMIDE $[\text{CO}(\text{NH}_2)_2]$

This important amide occurs as a normal constituent of urine, it being the chief form in which the waste or superfluous nitrogen of the system is eliminated. It may be regarded as a *diamide*, being derived from two molecules of ammonia by displacement of two out of the six atoms of hydrogen by the divalent radicle carbonyl (CO); thus:



The formula and constitution of urea are more conveniently represented by showing the bivalent carbonyl radicle (CO) in direct union with two equivalents of amidogen (NH₂), thus :

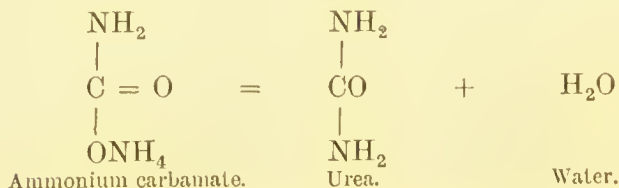


The relation of urea to carbonic acid and also to carbamic acid was illustrated on page 430, to which the student should refer.

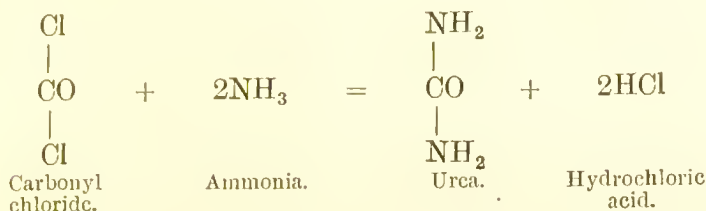
Preparation.—1. Urea may be extracted from urine by evaporating the urine to one-sixth of its bulk, and adding, when cold, strong nitric acid ; on standing, yellowish crystals of the nitrate of urea are deposited ; these are collected on a filter, dissolved in boiling water, and barium carbonate added to form barium nitrate and free urea. The whole is then evaporated to dryness on a water-bath, and the dry residue exhausted with boiling alcohol, which dissolves out the urea, leaving the barium nitrate insoluble ; the filtered alcoholic solution, when evaporated, deposits crystals of urea.

2. Urea may be prepared from its isomer ammonium cyanate by simply evaporating a solution of that salt to dryness on a water-bath (*see* page 526).

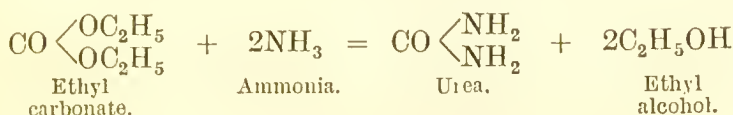
3. Urea is obtained by heating ammonium carbamate, so as to deprive it of the elements of water.



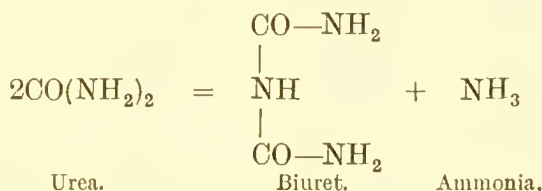
4. Urea can also be obtained by the action of ammonia on carbonyl chloride (COCl_2) (*see* page 208).



5. Urea is also produced by acting on ethyl carbonate [$(\text{C}_2\text{H}_5)_2\text{CO}_3$] with ammonia.



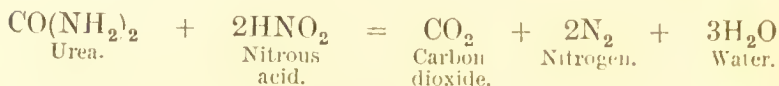
Properties.—Urea occurs in transparent colourless crystals, soluble in water and alcohol; under the influence of heat it evolves ammonia, producing at first biuret—



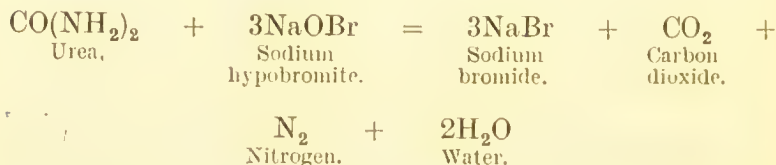
then cyanuric acid, and finally cyanic acid (*see* page 527). Urea is neutral to test-paper, but if urine is exposed to the air it soon becomes alkaline (owing to the action of bacteria), from conversion of the urea into ammonium carbonate, which is formed by the union of urea with the elements of water.



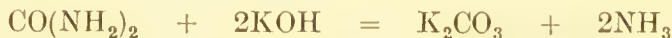
Urea is instantaneously decomposed by nitrous acid, carbon dioxide and nitrogen being evolved.



It is also decomposed by the hypobromites and hypochlorites with evolution of carbon dioxide and nitrogen; thus sodium hypobromite (NaOBr) in presence of urea is reduced to sodium bromide (NaBr), its oxygen oxidising the carbon and hydrogen of the urea to carbon dioxide and water respectively, the nitrogen being set free.



Caustic potash acts on urea, as on all amides, evolving ammonia and forming the potassium salt of the related acid (*see* page 429).



Estimation of urea in urine.—*Hypobromite process.*—This process consists in decomposing the urea in a measured quantity of urine by means of sodium hypobromite, an excess of free caustic soda being present in the hypobromite solution, so that the carbon dioxide is absorbed by it, and only the nitrogen is evolved; the volume of nitrogen evolved is then measured. The apparatus (Fig. 46) consists of a bottle A, into which 25 c.c. of a strong alkaline solution of sodium hypobromite is introduced; into this is carefully lowered a small test-tube *b* containing 5 c.c. of the urine to be examined, care

being taken not to spill any of the urine into the hypobromite solution. The bottle A is then connected by means of a perforated cork and india-rubber tubing with the graduated tube B, which is immersed in a reservoir of water C; before the com-

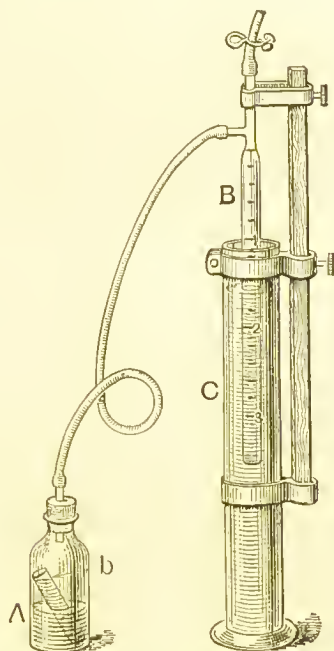


Fig. 46.—Apparatus for the estimation of urea in urine by the hypobromite process.

mencement of each experiment, the water level is adjusted so as to be at the zero mark on B.

The bottle A is then inclined to one side, so as to allow the urine contained in the small tube *b* to flow into the hypobromite solution, when the urea is immediately decomposed into carbon dioxide, nitrogen, and water; the carbon dioxide is instantly absorbed by the caustic soda present in the solution, and only the nitrogen escapes, with effervescence. Whatever the amount of nitrogen evolved, there

will be an equal volume of the air contained in the apparatus forced over into the measuring tube B, where the amount can be read off, after cooling by lowering B into the water in C, and then raising B until the water in B and C is at the same level. From this volume, the amount of urea contained in the 5 c.c. of urine can be determined. Employing 5 c.c. of urine for each estimation, the tube B is so graduated that the numbers 1, 2, 3, etc., marked on it represent 1, 2, and 3 per cent. of urea in the urine.

Tests.—If a crystal of urea be heated in a test-tube till ammonia is freely evolved, and the resulting biuret be then dissolved in a little warm water, on adding to the solution two or three drops of caustic potash and then one drop of copper sulphate solution a characteristic rose-violet colour will be obtained. This is the most satisfactory test for urea and is known as the biuret test.

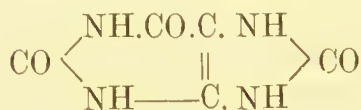
A *solution* of urea gives (1) a white precipitate with a solution of mercuric nitrate ;

(2) An effervescence of nitrogen with an alkaline solution of sodium hypobromite ;

(3) If moderately strong, crystals of urea nitrate, when mixed in the cold with strong nitric acid.

Closely associated with urea are **uric acid** and certain amino-acids, which represent, under normal or abnormal conditions, earlier stages in the manipulation of nitrogenous material in the body.

URIC ACID ($C_5H_4N_4O_3$), OR



This acid, formerly also called lithic acid, is a normal constituent of urine. *Sodium biurate* constitutes the gouty concretions in joints known as

chalk-stones. Ammonium urate is the chief constituent of the solid excrement of snakes.

Uric acid can be prepared from urine by acidifying with hydrochloric acid, when the uric acid separates out in crystals. It can be obtained in a purer state by boiling boar's excrement with potash, filtering and pouring the filtrate into dilute hydrochloric acid, when the uric acid is precipitated as a white powder. It has also been prepared artificially by heating glycocoll with urea. It is not a carboxylic acid, but acts like a weak dibasic acid. It is almost insoluble in water. The acid is soluble in caustic potash and caustic soda. It is closely related to the alkaloids, theobromine and theine.

Test.—If a few drops of strong nitric acid be added to some solid uric acid in a dish, and heat gently applied until all the nitric acid is driven off, a reddish-coloured residue (alloxan) will be left. If, when the dish is cold, a few drops of solution of ammonia are added to this, a beautiful crimson colour is developed, due to the production of murexide by the action of the ammonia on alloxan. This test for uric acid is, on that account, known as the *murexide* test.

AMINO-ACIDS

These acids are true carboxylic acids, but in the radicle which accompanies the carboxyl group a hydrogen atom has been replaced by amidogen (NH_2) (see page 494).

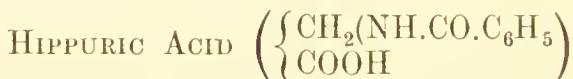
GLYCOCINE, GLYCINE, GLYCOCOLL, OR AMIDOACETIC



This body may be obtained by the action of ammonia on chloroacetic acid.



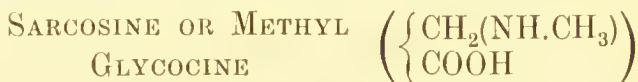
Glycocine enters into the composition of hippuric acid and of glycocholic acid, one of the bile acids. It is a solid crystalline substance with a sweetish taste, soluble in water.



Is benzamidoacetic acid, and is resolved by boiling with strong hydrochloric acid into benzoic acid (*see* page 547) and glycocine. It can be prepared from cows' and horses' urine by boiling with lime, filtering, and pouring the filtrate into hydrochloric acid.

GLYCOCHOLIC ACID

Present as sodium glycocholate in bile; is a compound of glycocine and cholic acid; by boiling glycocholic acid with hydrochloric acid it splits up into glycocine and cholic acid.



This body is glycocine, from which one atom of hydrogen of the amidogen has been displaced by methyl. Since glycocine is prepared by acting on chloracetic acid with ammonia, so sarcosine may be made by acting on chloracetic acid with methylamine, that is, with ammonia from which one atom of hydrogen has been displaced by methyl.



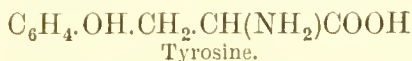
Sarcosine is not met with in the animal body, but is a product of the decomposition of creatine.

ALANINE $[\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}]$

This substance is α amino-propionic acid. It is accordingly converted by nitrous acid into lactic acid with evolution of nitrogen (*see* page 428).

TYROSINE $(\text{C}_9\text{H}_{11}\text{NO}_3)$

This body consists of alanine from which one atom of hydrogen of the CH_3 group has been displaced by the radicle hydroxyphenyl ($\text{C}_6\text{H}_4\text{OH}$).



Tyrosine is occasionally found in the urine together with leucine in connection with certain diseases of the liver; they are also both found among the products of pancreatic digestion.

LEUCINE $[(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}(\text{NH}_2)\text{COOH}]$

This compound is really α amino-isobutyl acetic acid. It is a product of the putrefaction of proteins, and can be obtained together with tyrosine from horn shavings.

Leucine is occasionally found in the urine in connection with certain diseases of the liver; it is one of the antecedents of urea.

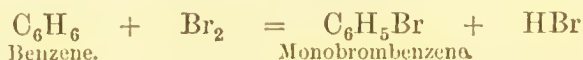
CHAPTER X

AROMATIC COMPOUNDS

Benzene—Toluene—Benzene Sulphonic Acid—Nitrobenzene—Aniline—Phenol—Phenol Sulphonic Acid—Picric Acid—Resorcin—Pyrogallic Acid—Benzaldehyde—Benzoic Acid—Hippuric Acid—Salicylic Acid—Gallic Acid—Tannin—Terpenes—Camphor.

THE **aromatic** or **closed-chain** bodies present a remarkable contrast in many of their reactions and properties to the fatty or open-chain bodies which we have discussed in the previous pages. As the latter may be looked upon as the derivatives, more or less direct, of marsh gas, so the aromatic bodies may be considered as derivatives of the hydrocarbon benzene. Many of them have fragrant odours, as oil of bitter almonds, nitrobenzene, benzoic acid, etc.; hence the name of *aromatic* bodies.

The molecular formula of **benzene** is C_6H_6 , whereas that of the 6-carbon paraffin is C_6H_{14} . Benzene must therefore be an eminently unsaturated hydrocarbon, and should readily add on eight bromine atoms, for instance. We find, however, that when the two liquids are mixed together, a substitution compound is formed, and hydrobromic acid evolved, the action being completed on heating, thus:



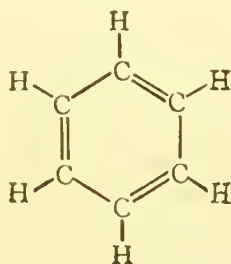
When only the vapour of bromine is allowed to come into contact with the benzene, and the action

is allowed to proceed for days, in sunlight, at ordinary temperature, an addition compound is formed, but the maximum number of bromine atoms ever added on is six, forming the compound $C_6H_6Br_6$. We must therefore conclude that the structure of benzene in some way provides two valencies fewer than the paraffin structure. This will be the case if the two ends of the paraffin open chain are connected together so as to form a closed circuit of some sort.

The conversion of acetylene to benzene (*see* page 448) suggests that benzene contains only CH groups, and this is completely confirmed by the absence of isomeric varieties of any of its mono-derivatives.

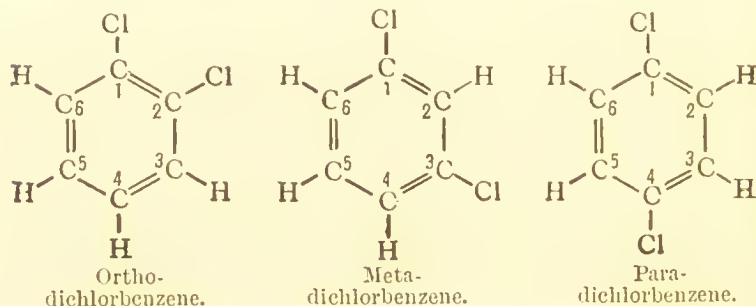
Any structural formula suggested for benzene must be consistent with these established facts; the one usually adopted was proposed by Kekulé in 1865. The projection of it on a plane surface shows the six carbon atoms arranged at the six angles of a hexagon, and, alternately, doubly and singly linked. The remaining six valencies are engaged with the six hydrogen atoms.

It is obvious that the second valency between alternate carbon pairs is really superfluous, and satisfies arithmetical, rather than chemical, requirements. They are really employed to form addition compounds.



Kekulé's ring formula
for benzene.

This formula explains most of the reactions of benzene; for instance, as all the hydrogen atoms are similar, if we replace *one* hydrogen atom by chlorine or bromine, the resulting monochlorobenzene will be the same in every case; accordingly only one monochlorobenzene is known. If, however, we replace *two* atoms of hydrogen by two atoms of chlorine, in such a formula, three modifications are possible, and only three:—

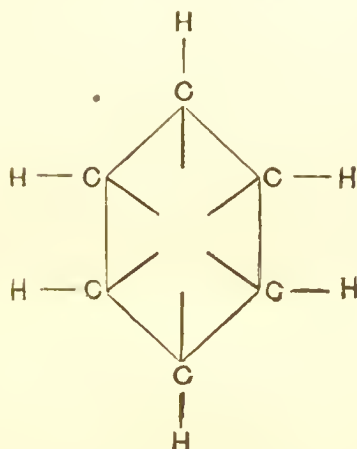


Accordingly we find three, and only three, dichlorobenzenes known. These are generally named 1·2 ortho (o), 1·3 meta (m), and 1·4 para (p) derivatives.

If a third atom of hydrogen is replaced by chlorine, three different trichlorobenzenes can be obtained; these are known, and are distinguished as *consecutive* (1, 2, 3), *symmetrical* (1, 3, 5), and *irregular* (1, 2, 4). Inspection of the graphical formulæ of the three di-derivatives shows that only the *meta* variety can yield all three tri-derivatives. The *ortho* variety can only yield two of them (consecutive and irregular), while the *para* yields only the irregular arrangement wherever the third chlorine atom is placed. In this way the *orientation*, as it is called, of a di-derivative may be determined.

Another structural formula for benzene has been proposed by Armstrong and by Baeyer. It is known as the *centric* formula, and represents the fourth

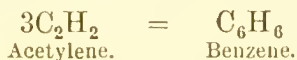
bonds of the carbon atoms as *directed* in an indefinite sort of way to the centre without being actually united.



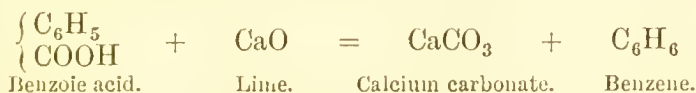
Centric formula of benzene.

Benzene, often called benzol, can be prepared—

1. By heating acetylene to redness in a tube of hard glass.



2. By distilling benzoic acid with lime.



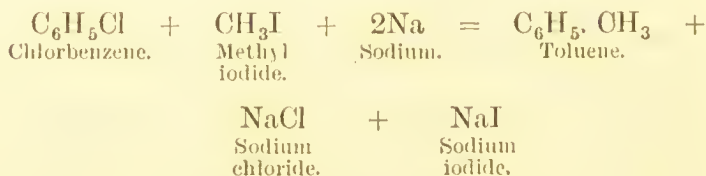
3. On the large scale it is manufactured from coal tar. When coal tar is subjected to fractional distillation, the portion which comes over below 170° is known as "light oil"; on fractionating this light oil, the portion which distils over below 140° contains the benzene. This portion is treated consecutively with dilute sulphuric acid and with caustic soda, and repeatedly washed; the neutral oil is then distilled, and the portion coming over

between 80° – 90° collected; it is then cooled to -12° , pressed, and finally distilled, the portion boiling 80° – 81° being almost pure benzene.

Properties.—Benzene is a thin, colourless, limpid liquid, with a peculiar odour. Its specific gravity is $\cdot 885$; it boils at 80.5° ; solidifies at 6° . It is very inflammable, burning with a smoky flame on account of the large amount of carbon it contains. It is a powerful solvent of fats, and is on this account commonly employed for removing grease; it is almost insoluble in water, but mixes readily with alcohol and ether.

TOLUENE OR METHYL BENZENE ($C_6H_5.CH_3$)

This body is commonly known as *toluol*. It is contained in the coal-tar distillate, and passes over between 100° and 120° . It is a liquid, smelling like benzene, and may be obtained by the substitution of methyl for chlorine in chlorbenzene. This is effected by distilling together chlorbenzene, methyl iodide, and sodium.

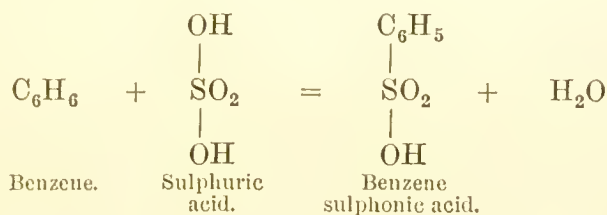


Toluene forms two types of derivatives. Those formed by substitution in the C_6H_5 , or *ring*, are aromatic compounds and resemble the benzene derivatives; but those formed by substitution in the CH_3 , or *side chain*, rather resemble the methyl and ethyl derivatives, which also arise from substitution in a CH_3 group. Thus benzyl alcohol, $C_6H_5.CH_2OH$, has the characteristic class group of a primary alcohol, and accordingly resembles ethyl

alcohol in general features. On oxidation it forms benzoic aldehyde, $C_6H_5.CHO$, and benzoic acid, $C_6H_5.COOH$, just as alcohol forms acetic aldehyde and acetic acid.

BENZENE SULPHONIC ACID ($C_6H_5.SO_2OH$)

Concentrated sulphuric acid converts benzene into benzene *sulphonic acid*. In these acids the hydrocarbon radicle has replaced the whole hydroxyl group of sulphuric acid, and not merely a hydrogen atom as in the sulphovinic acids; thus:



The hydrogen atom of the remaining hydroxyl group may be replaced by potassium, etc., forming *sulphonates*.

NITROBENZENE ($C_6H_5NO_2$)

This body is also known as *nitrobenzol* and *essence of mirbane*. It is obtained by the action of strong nitric acid (with strong sulphuric acid) on benzene, the mixture being subsequently poured into water.

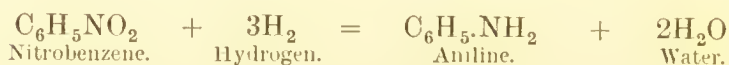


Properties.—Nitrobenzene is a yellow liquid of specific gravity 1.2, and boils at 205° . It possesses a strong odour resembling that of the *essential oil of bitter almonds*, and is on this account used for

flavouring and perfuming, although it is a poisonous substance. It is also extensively employed in commerce in the manufacture of aniline. Dinitro [$\text{C}_6\text{H}_4(\text{NO}_2)_2$] and trinitro [$\text{C}_6\text{H}_3(\text{NO}_2)_3$] benzenes have also been prepared.

ANILINE, OR PHENYLAMINE ($\text{C}_6\text{H}_5\text{NH}_2$)

This important amine is prepared by the action of reducing agents on nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$); this is generally carried out by exposing nitrobenzene to the action of iron filings and acetic acid.



Aniline, when first prepared, is a colourless liquid, boils at 184.5° , specific gravity 1.036; it gradually assumes a brownish colour on exposure to air. Aniline acts as a strong base of the ammonia type, forming salts by addition. When acted upon by oxidising substances it furnishes a number of coloured bodies, well known as aniline dyes.

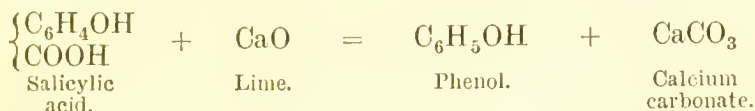
Heated with solid mercuric chloride, aniline forms a dark-red* mass, soluble in alcohol to a magenta-coloured solution.

Heated with chloroform, alcohol, and caustic potash, aniline produces a body of extremely disagreeable odour—phenyl isocyanide ($\text{C}_6\text{H}_5\text{NC}$); this can be used as a test for chloroform or aniline (*see* page 432).

Although almost insoluble in plain water, aniline readily dissolves in dilute acids, as the aniline salts are soluble in water. A solution of the hydrochlorate, even when very dilute, shows a fine mauve colour on addition of a few drops of solution of bleaching powder.

PHENOL, OR CARBOLIC ACID (C_6H_5OH)

This body, which is the ordinary carbolic acid, is also known as *phenic acid*. It is contained in coal tar, from which it is obtained for commercial purposes from that portion of coal tar distilling between 180° and 190° . It may be obtained in a chemically pure state by the withdrawal of carbon dioxide from salicylic acid, which is effected by heating salicylic acid with quicklime.



Nitrons acid converts aniline into phenol (*see* page 428).

Properties.—Carbolic acid is, in the pure state, a colourless crystalline body, but it soon assumes a pink colour. It is soluble in 15 parts of water, and readily soluble in alcohol, ether, and glycerin (*glycerinum acidi carbolici*). If solid carbolic acid is mixed with a small quantity of water it liquefies, 100 parts of the acid and 10 parts of water forming *acidum carbolicum liquefactum*. It possesses a characteristic odour and taste, somewhat resembling creosote. It is a powerful antiseptic on account of its germicidal properties. It is a corrosive and irritant poison. It will be noticed that phenol is the hydroxide of the radicle phenyl (C_6H_5), just as ordinary alcohol is the hydroxide of the radicle ethyl (C_2H_5); it differs, however, from ordinary alcohol in many respects, and is perhaps more akin to an acid in its character; it dissolves readily in potassium hydrate, forming a carbolate or phenate (C_6H_5OK); it does not contain the group (CH_2OH) characteristic of a primary alcohol, and so yields, on

oxidation, no bodies comparable to aldehyde and acetic acid. On the other hand, it is not a true acid, and does not contain the group (COOH). It is, in fact, the type of a new class of compounds which are called *phenols*. We now distinguish three kinds of hydroxyl groups—alcoholic, acidic, and phenolic.

Tests. — 1. Carbolic acid gives, with bromine water, a white precipitate of tribromphenol ($C_6H_2Br_3OH$). This constitutes a very delicate test for carbolic acid, and is the best method for its detection in the urine in cases of carbolic-acid poisoning, and in cases of absorption of carbolic acid from wounds washed with carbolic-acid lotion. 2. Ferric chloride gives with a solution of carbolic acid a violet colour, which is discharged by dilute acetic acid.

PHENOL SULPHONIC ACID [$C_6H_4(OH)SO_3H$]

This is prepared by dissolving carbolic acid in strong sulphuric acid. By mixing it with metallic hydroxides or carbonates, sulphonates are formed. Two of these salts are used in medicine, viz. sodium sulphocarbolate [$C_6H_4(OH)SO_3Na$], and zinc sulphocarbolate.

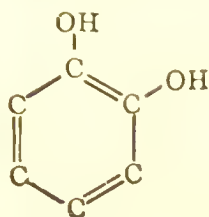
TRINITROPHENOL OR PICRIC ACID [$C_6H_2(NO_2)_3OH$]

This is obtained by dropping carbolic acid into fuming nitric acid. It forms yellow crystals, known as *carbazotic acid* or *picric acid*; it is very bitter; its salts are explosive; it is used as a dye.

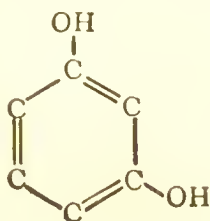
RESORCIN [$C_6H_4(OH)_2$]

Three metameric dihydroxybenzenes exist (page 538), according to the relative positions of the

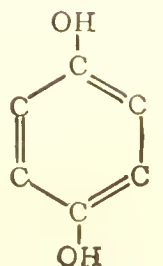
hydroxyl groups in the benzene ring, viz. (the hydrogen atoms are omitted) :



(*ortho*)
Catechol
(or pyrocatechin).



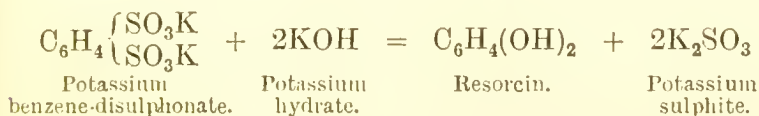
(*meta*)
Resorcinol.



(*para*)
Hydroquinone.

Of these, only the meta derivative is used in medicine.

Resorcinol or resorcin is prepared by fusing benzene disulphonate of potassium with caustic potash.

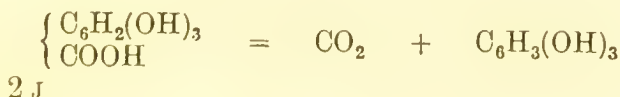


It is a white crystalline substance, soluble in water, alcohol, and ether. It gives a dark-violet colour with ferric chloride, and a white precipitate with bromine water.

The *para* derivative, hydroquinone, is largely used as a developer in photography.

PYROGALLOL, OR PYROGALLIC ACID

This is a trihydroxybenzene (the OH groups being in the positions 1, 2, 3); it sublimes when gallic acid is heated.



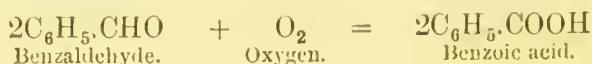
It forms colourless, very light crystals, melting at 115° , and very soluble in water; when mixed with an alkaline hydrate the solution absorbs oxygen, rapidly turning almost black.

BENZOIC ALDEHYDE, BENZALDEHYDE, OR ESSENTIAL OIL OF BITTER ALMONDS ($C_6H_5\cdot CHO$)

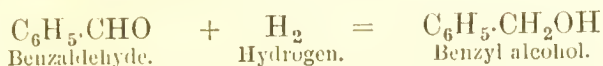
This was obtained from the glucoside amygdalin present in the bitter almond seeds, by digesting the bitter almonds with water and afterwards distilling. The almond seeds contain a ferment *emulsin* or *synaptase*, which, in presence of water, causes the amygdalin to decompose into the essential oil of bitter almonds, hydrocyanic acid, and glucose (*see* page 489).

The essential oil of bitter almonds thus prepared contains a considerable quantity of hydrocyanic acid (4 to 8 per cent.), unless specially purified from it. It may be freed from the hydrocyanic acid by distillation with slaked lime and ferrous chloride, by which means the volatile hydrocyanic acid is converted into the non-volatile calcium ferro-cyanide.

The aldehyde is now prepared by hydrolysing benzyl chloride ($C_6H_5CH_2Cl$) to benzyl alcohol ($C_6H_5CH_2OH$) by boiling with water and lead nitrate. The nitrate then oxidises the alcohol to aldehyde with formation of oxides of nitrogen, which are immediately removed by a current of CO_2 . If the essential oil of bitter almonds is exposed to the air it absorbs oxygen, the benzoic aldehyde becoming converted into benzoic acid, which is deposited as white crystals.



When reduced by sodium amalgam, benzaldehyde forms benzyl alcohol.



Benzaldehyde is a thin, colourless liquid; specific gravity 1.05; boils at 180° ; it does not reduce Fehling's copper solution; it does, however, reduce ammoniacal silver nitrate, and resembles acetic aldehyde in most of the general reactions already tabulated (*see* page 491). With caustic potash, however, no resin is formed, but benzyl alcohol and potassium benzoate, thus:

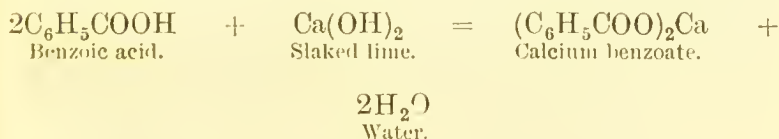


With ammonia no addition compound corresponding to aldehyde ammonia is formed, but more complex products—*c.g.* hydrobenzamide.



BENZOIC ACID ($\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{OH}$)

This acid may be prepared (1) from gum benzoin, which contains from 12 to 15 per cent. of it, by heating the crushed benzoin, when the benzoic acid sublimes; or more economically by boiling the crushed benzoin with slaked lime and water, when the benzoic acid is extracted as the soluble calcium benzoate.

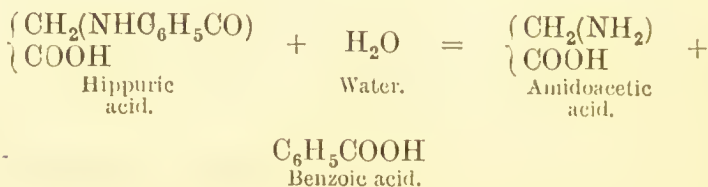


From the filtrate benzoic acid is precipitated by the addition of hydrochloric acid.

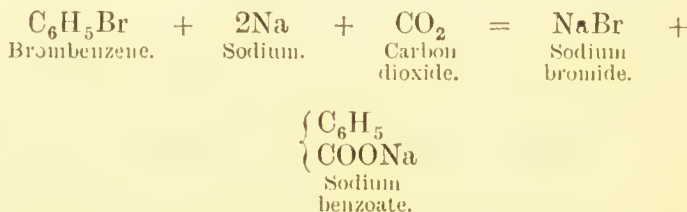


(2) Benzoic acid may be prepared by the oxidation of oil of bitter almonds (*see* page 546).

(3) Benzoic acid may also be obtained from hippuric acid (*see* page 534), by boiling that acid with hydrochloric acid, when it takes up a molecule of water.



(4) By the action of sodium and carbon dioxide on monobrombenzene.

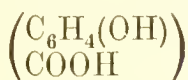


Benzoic acid forms glistening crystals with a characteristic odour, slightly soluble in water, melting at 120°, subliming at 125°. The vapour produces violent coughing.

In neutral solutions of benzoates—

1. Dilute hydrochloric acid produces a white precipitate of benzoic acid, easily soluble in ether.
2. Neutral ferric chloride solution produces a flesh-coloured precipitate of ferric benzoate.

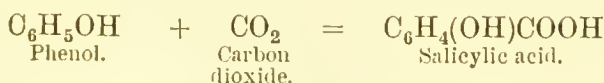
SALICYLIC ACID OR ORTHO-HYDROXY-BENZOIC ACID



Two kinds of salicylic acid occur in commerce, namely, the *natural* and *artificial* salicylic acids. The natural salicylic acid is obtained from oil of winter green or methyl salicylate, by distilling it with caustic soda, when methyl alcohol distils over and sodium salicylate is left behind. If the sodium salicylate is dissolved in water, salicylic acid can be precipitated by the addition of hydrochloric acid to the solution. Artificial salicylic acid is prepared from phenol. As ordinary phenol sometimes contains

cresol, the poisonous creosotic acid $\left\{ \begin{array}{c} \text{C}_6\text{H}_3\text{CH}_3\text{OH} \\ \text{COOH} \end{array} \right\}$

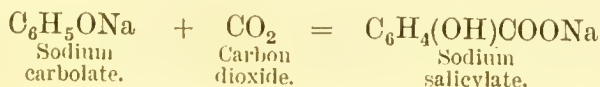
may also be formed. On this ground the natural salicylic acid is still sometimes preferred for medical purposes. It will be seen that if carbon dioxide is added to the molecule of phenol, salicylic acid is produced, thus:



This is effected by (1) converting the phenol into sodium carbolate by the addition of caustic soda—



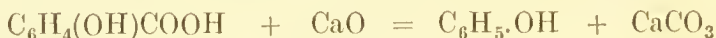
(2) saturating the dry sodium carbolate with carbon dioxide under pressure; (3) finally heating the product to about 130°, when it becomes converted into sodium salicylate. Expressed as one reaction, the change is—



Salicylic acid is precipitated from an aqueous solution of the sodium salicylate by the addition of hydrochloric acid.

Properties.—Salicylic acid is a white, crystalline solid, free from smell, slightly soluble in cold water and readily soluble in hot water, alcohol, and ether. The pure acid melts at 157° . It is an antiseptic. It is largely used in medicine in the form of its sodium salt, the preparation of which has been described in the two processes given above.

Tests.—1. Salicylic acid heated with quicklime evolves the odour of carbolic acid—

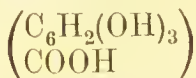


2. In aqueous solutions of the acid or its salts—

(a) Ferric chloride solution produces a violet colour which is *not* discharged by dilute acetic acid.

(b) Bromine water produces a white precipitate of tri-brom salicylic acid.

GALLIC ACID OR TRIHYDROXYBENZOIC ACID



Gallic acid occurs in small quantity in oak galls, but is generally prepared from tannic acid by the union of that body with the elements of water. As tannic acid is contained to a considerable extent in oak galls, gallic acid is prepared by boiling the crushed galls with dilute sulphuric acid for about half an hour, when the tannin unites with the elements of water and forms gallic acid. If the liquid is filtered while hot, it deposits crystals of gallic acid on cooling.

Tests.—In a solution of gallic acid (1) ferric chloride produces a bluish-black precipitate of ferric

gallate; (2) potassium cyanide solution produces a fine rose colour, which soon fades, but returns on shaking the liquid.

TANNIN, OR TANNIC ACID ($C_{14}H_{10}O_9$)

This substance is a constituent of oak galls, from which it is obtained by macerating the galls in a mixture of ether, alcohol, and water. The strained aqueous liquor, if evaporated, deposits tannin. The relationship of tannin to gallic acid is represented in the following equation, which shows that two molecules of gallic acid, deprived of one molecule of water, yield tannin.



Tests.—In a solution of tannic acid (1) ferrie ehloride produces a dark bluish-black precipitate of ferrie tannate resembling in appearance the precipitate of ferrie gallate. (2) An aqueous solution of gelatine becomes precipitated. This test serves to distinguish tannic acid from gallic acid, as the latter does not precipitate gelatine.

TERPENES

Terpenes of the formula $C_{10}H_{16}$ are isomeric hydrocarbons occurring as volatile oils in plants, from which they may be obtained by a process of distillation. The commonest terpene is oil of turpentine; other terpenes isomeric with this are the volatile or essential oils of lemon, orange, citron, and bergamot.

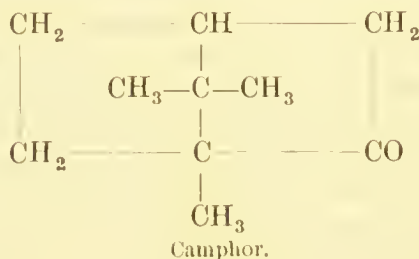
ESSENTIAL OIL OF TURPENTINE ($C_{10}H_{16}$)

Is also known as oil of turpentine, spirits of turpentine, turpentine, and "turps." It is pre-

pared by distillation from the crude turpentine or oleo-resin, obtained from various species of pine trees; the volatile oil of turpentine distils over, and common resin is left in the retort. The chief constituent of the oil is the closed chain hydrocarbon pinene ($C_{10}H_{16}$) which boils at 156° .

CAMPHOR ($C_{10}H_{16}O$)

Closely associated with the terpenes are camphor and its numerous relatives. Indeed, pinene hydrochlorate ($C_{10}H_{16}HCl$) has long been known as "artificial camphor" from its resemblance to the natural substance. The latter, however, contains no chlorine, and is really a ketone having the graphical formula—



Borneo camphor is the corresponding secondary alcohol.

Camphor is a colourless, transparent, crystalline solid, but has a somewhat tough and fibrous texture. It is a volatile substance, and is easily obtained from the leaves and bark of the camphor tree by steam distillation; crude camphor can also be purified by sublimation. It melts at 175° and boils at 205° . It is included in various medicinal preparations.

CHAPTER XI

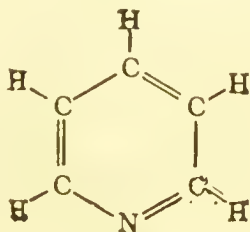
ALKALOIDS AND OTHER SUBSTANCES OF MEDICINAL INTEREST

VEGETABLE ALKALOIDS

These bodies act like organic bases of the ammonia type, forming salts by addition. Their aqueous solutions have also an alkaline reaction to litmus. To this resemblance the name "alkaloid" is due, from *alkali*, and εἶδος, likeness. All alkaloids contain nitrogen, and are in fact, derivatives of ammonia, the hydrogen of which has been partially or entirely displaced by various radicles. They are closely related to the tertiary amines.

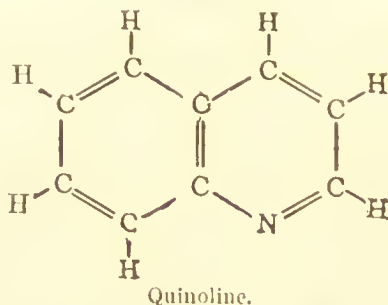
Most alkaloids are solid, crystalline, and non-volatile. Conine and nicotine are volatile liquids, and contain no oxygen. These have been prepared synthetically, as also theobromine, thein, and others, but the constitution of many is still unknown.

Some appear to be derivatives of pyridine, a liquid found in coal tar and in bone oil. This compound may be regarded as benzene, in which one of the CH groups is replaced by nitrogen.



Pyridine.

Some, as the quinine alkaloids, are closely connected with quinoline, an oil also found in coal tar and bone oil, which may be looked upon as two benzene rings, having two carbon atoms in common, in which one CH group has been replaced by one atom of nitrogen.



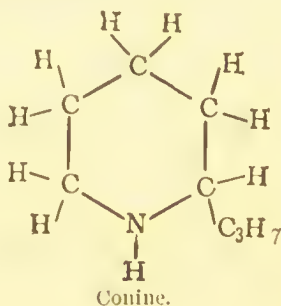
Group tests.—In aqueous solutions of alkaloids acidulated with dilute sulphuric acid—

1. Solution of iodine in potassium iodide produces a brown precipitate.

2. Phosphomolybdic acid produces a yellowish precipitate.

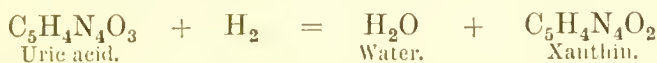
CONINE ($C_8H_{17}N$)

Is contained in the seeds of the hemlock, from which it can be obtained by distillation with caustic soda; it is a colourless oil, boiling at 167° and readily soluble in water. It has been prepared artificially and shown to be an iso-propyl (C_3H_7) derivative of piperidine:



THEOBROMINE ($C_7H_8N_4O_2$), THEIN, OR CAFFEIN
($C_8H_{10}N_4O_2$)

These alkaloids can be prepared from uric acid (see page 532), to which they are closely related. Theobromine is the essential alkaloid in cocoa. Thein and caffeine (which seem to be identical) are found in tea and coffee. If uric acid be treated with sodium amalgam, one atom of oxygen is replaced by an atom of hydrogen, and an atom of hydrogen is removed, a new substance, xanthin, being formed.



By subjecting xanthin to a well-known process, two atoms of hydrogen are replaced by two methyl (CH_3) groups, and we have dimethylxanthin or theobromine [$C_5H_2(CH_3)_2N_4O_2$]; by repeating the process another hydrogen is similarly replaced and trimethylxanthin or thein [$C_5H(CH_3)_3N_4O_2$] is formed.

MORPHINE, OR MORPHIA ($C_{17}H_{19}NO_3$, H_2O)

This alkaloid exists in opium in combination with meconic acid as *meconate of morphine*; a fair sample of opium contains from 8 to 12 per cent. of morphine. It is extracted by the following process:—

1. The opium is macerated in water and exhausted by percolation, by which means an aqueous extract of the meconate of morphine is obtained.

2. To this aqueous extract calcium chloride is added, when the meconic acid is precipitated as calcium meconate, the soluble hydrochlorate of morphine remaining in solution.

3. The liquid is filtered, and the filtrate, containing the hydrochlorate of morphine, is decolorised by boiling with animal charcoal.

4. The liquid is filtered from the animal charcoal, and evaporated to a low bulk; it is then set aside to cool, when it deposits crystals of the hydrochlorate of morphine.

5. To obtain the free alkaloid, solution of ammonia is added to a strong aqueous solution of the hydrochlorate, when the morphine is thrown down as a white precipitate, the ammonia uniting with the hydrochloric acid.

The constitution of morphine has been the subject of much investigation. It contains two hydroxyl groups, one alcoholic, and one phenolic; to the latter it owes two properties which are generally associated with this group, namely (1) solubility in caustic alkalis and (2) the property of producing a colour with ferric chloride solution.

Morphine hydrochlorate, or hydrochlorate of morphia ($C_{17}H_{19}NO_3, HCl$).—This compound is prepared in the process just described.

Morphine acetate, or acetate of morphia ($C_{17}H_{19}NO_3, CH_3.COOH$).—This compound is prepared by dissolving the free alkaloid (precipitated by ammonia from the hydrochlorate) in acetic acid. Morphine acetate is the salt generally employed for hypodermic injection.

Tests for morphine.—1. Ferric chloride produces a dingy-blue colour in a neutral solution of a morphine salt. In the cases of the acetate and meconate of morphine, this blue colour is more or less masked by the production of the red colour that ferric chloride gives with an acetate and meconate.

2. Strong nitric acid gives an orange-red colour with morphine and its salts; this colour can also be obtained by the addition of sufficient nitric acid to a strong solution of a morphine salt.

3. Sulphomolybdic acid (made by warming strong H_2SO_4 with a little solid Am_2MoO_4), rubbed with

morphine or any of its salts in the solid state, gives a dark-crimson colour, changing after a short time to a sapphire blue; this constitutes a very delicate test for morphine.

Detection of opium.—Apart from its characteristic smell, analytical evidence of the presence of opium is gained by obtaining the reactions for morphine (as detailed above) and for meconic acid. The reaction for meconic acid is that it gives a blood-red colour with ferric chloride, which colour is not discharged either by the addition of hydrochloric acid or of solution of mercuric chloride; this distinguishes it from similar red colours given by ferric chloride with acetates and sulphocyanides (see pages 499, 525).

APOMORPHINE ($C_{17}H_{17}NO_2$)

The molecule of this body differs from that of morphine by containing one molecule of water less. It is prepared by heating morphine with strong hydrochloric acid, when the elements of water are withdrawn from the morphine, and the hydrochlorate of apomorphine remains. This alkaloid possesses physiological properties entirely different from those of morphine; it is a very powerful and rapid emetic, and has none of the narcotic properties of morphine and its salts.

CODEINE ($C_{18}H_{21}NO_3, H_2O$)

This is one of the alkaloids of opium; it is closely related to morphine, being *Methyl morphine*; that is, it consists of morphine, from the molecule of which one atom of hydrogen has been displaced by the radicle methyl, as shown in the following formulæ:

Morphine— $C_{17}H_{19}NO_3, H_2O$.

Codeine or methyl morphine— $C_{17}H_{18}(CH_3)NO_3, H_2O$.

QUININE, OR QUINIA ($C_{20}H_{24}N_2O_2, 3H_2O$)

This, together with other alkaloids, exists in the different cinchona barks, from which it may be extracted by the following process :

1. The powdered cinchona bark is exhausted by percolation with water acidulated with hydrochloric acid, by which means the quinine is removed in solution as hydrochlorate of quinine.

2. The solution is decolorised by means of animal charcoal.

3. The quinine is precipitated from the solution of the hydrochlorate by the addition of caustic soda, which sets free the quinine as a white precipitate, by uniting with the hydrochloric acid to form sodium chloride.

Sulphate of quinine.—This is the form in which quinine is generally employed in medicine ; it is made by dissolving the precipitated quinine in dilute sulphuric acid. The commercial sulphate of quinine, or *disulphate of quinine*, as it is sometimes called, has the composition $(C_{20}H_{24}N_2O_2)_2, H_2SO_4$; it is only slightly soluble in water, but may be readily dissolved by the addition of a little dilute sulphuric acid, which forms the so-called neutral or soluble sulphate $(C_{20}H_{24}N_2O_2, H_2SO_4)$.

Tests for quinine.—1. If to a solution of a quinine salt some chlorine water and then solution of ammonia be added, a green colour will be produced.

2. If the above-mentioned test be repeated, adding some potassium ferrocyanide solution before the addition of the ammonia, a red colour will be produced.

Cinchonine, *cinchonidine*, and *quinidine* are alkaloids also present in cinchona barks.

Quinine and cinchonine are closely related. Quinine appears to be methoxy cinchonine ; quinine is lævorotatory, cinchonine is dextrorotatory.

STRYCHNINE OR STRYCHNIA ($C_{21}H_{22}N_2O_2$)

This alkaloid exists in *nux vomica* seeds in company with another alkaloid, *brucine* or *brucia*.

Strychnine is extracted by the following process :

1. The crushed seeds are exhausted by maceration and percolation with rectified spirit, and from the tincture so obtained the spirit is recovered by distillation.

2. The soft extract left, after the recovery of the spirit, is mixed with water, to precipitate resinous matters; acetate of lead is also added to throw down colouring matter, etc., leaving acetate of strychnine in solution.

3. The liquid is filtered from precipitated matters, and the filtrate is concentrated by evaporation; on the addition of ammonia, strychnine is precipitated, together with brucine.

4. To separate the brucine from the strychnine the precipitate is dissolved in alcohol, and the solution is evaporated to a low bulk; on setting it aside to cool, the strychnine crystallises out, leaving the more soluble brucine in solution in the mother liquid.

Test for strychnine.—If a little strong sulphuric acid be added to a fragment of strychnine placed on a white porcelain dish or plate, and the mixture be touched with a glass rod dipped in a solution of potassium bichromate in strong sulphuric acid (made by adding a crystal or two of the bichromate to a few drops of sulphuric acid), a beautiful dark-purple or violet colour will be developed, fading after a short time to a pale-red colour.

BRUCINE OR BRUCIA ($C_{23}H_{26}N_2O_4$)

The separation of this alkaloid from strychnine has been described in the process just given. Brucine appears to differ from strychnine in containing two

methoxyl (OCH_3) groups in place of two hydrogen atoms, and therefore to be $\text{C}_{21}\text{H}_{20}(\text{OCH}_3)_2\text{N}_2\text{O}_2$.

Test for brucine.—Strong nitric acid gives a bright blood-red colour with brucine and its salts. If the acid be evaporated away on the water-bath and the residue diluted with water, the addition of stannous chloride solution or sodium thiosulphate will turn the liquid (which is then yellow) to a fine purple colour.

RARER ALKALOIDS

Aconitine, atropine, cocaine, hyoscyamine, veratrine, etc., are prepared by separate processes, for a description of which the student is referred to special treatises. We shall, however, indicate in outline a method of general application.

General process for the extraction of alkaloids.—1. The crushed roots, bark, leaves, fruits, or seeds are exhausted by maceration and percolation with alcohol containing tartaric acid; tartrates of the alkaloids being soluble in alcohol.

2. The alcohol is recovered by distillation, and the soft extract left is mixed with water to precipitate resinous matters.

3. The liquid is filtered from precipitated resinous matters, and the alkaloid precipitated by the addition of sodium carbonate.

4. The precipitated alkaloid is purified by solution in, and crystallisation from, a suitable solvent, such as ether, chloroform, or alcohol. If necessary, colouring matter is removed from the alkaloid by means of animal charcoal.

LIQUID VOLATILE ALKALOIDS

Conine (contained in the conium or hemlock plant), nicotine (contained in tobacco), and pilocarpine (con-

tained in jaborandi leaves) are liquid volatile alkaloids ; they may all be prepared by distilling the part of the plant containing the alkaloid with a dilute solution of caustic potash, when the alkaloid is set free, and being volatile distils over.

PTOMAINES, OR ANIMAL ALKALOIDS

Ptomaines are alkaloids produced by the decomposition of animal substances. The word *ptomaine*, which is derived from $\pi\tau\tilde{\omega}\mu\alpha$, a corpse, and *inus*, belonging to, was at first restricted to alkaloids produced by cadaveric decomposition ; it is now also employed to designate alkaloids of animal origin formed during life as the result of chemical changes induced by some agency or other acting within the organism.

At the beginning of the last century the formation of alkaloids by plants was clearly established ; but until 1872 the power of producing alkaloids was believed to be restricted to plants, and not to be shared by animal organisms. Gautier, as the result of his researches on putrefying albuminous substances, was the first clearly to establish the fact that plants possess no monopoly of producing alkaloids, but that this productive power is equally shared by animal substances. The various forms of albumin are the common ancestors of alkaloids, whether animal or vegetable ; and it is by various changes in the albumin molecule that animal alkaloids are produced.

RARER ORGANIC SUBSTANCES USED IN MEDICINE

Acetanilide ($\text{CH}_3\text{CONH.C}_6\text{H}_5$), also known as *antifebrin* and *phenylacetamide*, may be regarded as acetamide (CH_3CONH_2) in which one atom of

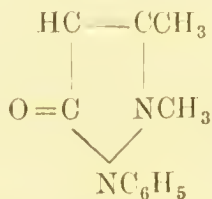
hydrogen in the NH_2 group has been replaced by the radicle phenyl (C_6H_5); or, it may be regarded as aniline in which one of the same hydrogen atoms has been replaced by acetyl (CH_3CO); it is obtained by the prolonged action of glacial acetic acid on pure aniline.



It forms colourless, odourless crystals, which melt at 115° and have a greasy feel and faint burning taste. Not very soluble in cold water, but soluble in alcohol, ether, and chloroform. Used as an antipyretic.

Test.—Boiled with solution of caustic potash acetanilide evolves the odour of aniline, and this on subsequent addition of chloroform and further heating gives place to the characteristic odour of phenyl isocyanide (see page 542).

Antipyrine, known in the B.P. as *phenazone*, is a somewhat complex benzene derivative prepared by the interaction of phenylhydrazine ($\text{NH}_2\text{NHC}_6\text{H}_5$) and ethyl aceto-acetate (see page 492), and subsequent methylation of the product. Its constitutional formula is—



It is a colourless, odourless, crystalline substance, melting at 110° , readily soluble in water, alcohol, and chloroform. In a dilute aqueous solution, addition of ferric chloride solution produces a deep-red colour. Used as an antipyretic.

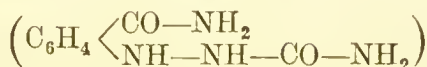
Argyrol.—A silver compound with a protein; used in mucous catarrh, and for the eye.

Aspirin $\left(\begin{array}{l} \text{C}_6\text{H}_4\text{OCH}_3\text{CO} \\ \text{COOH} \end{array} \right)$, *acetyl salicylic acid*, is used as an anti-rheumatic as a substitute for salicylic acid. Crystallises in white silky crystals.

Benzosol $[\text{C}_6\text{H}_4.\text{O}(\text{CH}_3).\text{O}(\text{C}_7\text{H}_5\text{O})]$ is *benzoyl-guaiacol* (see below), that is, one of the H atoms in guaiacol ($\text{C}_6\text{H}_4.\text{OCH}_3.\text{OH}$) has been replaced by the acid radicle benzoyl ($\text{C}_6\text{H}_5\text{CO}$). It is a colourless, crystalline powder, melts at 59° , is insoluble in water, soluble in ether and in chloroform. Used in cases of phthisis.

Chinosol.—The potassium salt of oxychinolin and sulphuric acid—a yellow crystalline powder. An antiseptic used in surgical dressing.

Cryogenin or Kryogenin



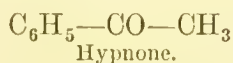
m. benzamido semicarbazide.—An antipyretic.

Formin (see Urotropine, page 567).

Guaiacol $[\text{C}_6\text{H}_4.\text{OH}.\text{O}(\text{CH}_3)]$, *methyl catechol* (see page 545), prepared from beechwood tar ereosote, is a coloured liquid of an agreeable odour; specific gravity 1.133; readily soluble in alcohol and ether.

Heroin $[\text{C}_{17}\text{H}_{17}\text{NO}(\text{OCH}_3\text{CO})_2]$, is diacetyl morphine; obtained, by heating the base with excess of acetic anhydride, in small glistening prisms; melts at 159° .

Hypnone.—Phenyl-methyl-ketone; that is, it consists of CO in union with the phenyl and methyl radicles; thus:



It is obtained, by distillation, from a mixture of benzoate of calcium and acetate of calcium. At

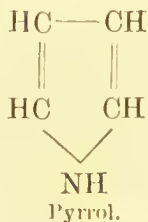
ordinary temperatures it is a colourless oily liquid, but below 14° it crystallises in white needles. It is insoluble in water, but soluble in alcohol.

Ichthyol $[(\text{NH}_4)_2\text{C}_{28}\text{H}_{36}\text{S}_3\text{O}_6]$.—An ammonium salt of sulpho-ichthyolic acid. It is obtained by treating the products of distillation of a bituminous quartz with sulphuric acid, and neutralising the sulpho-ichthyolic acid so produced with ammonia. The strata from which the bituminous quartz is obtained contain the remains of fishes and other animals, and the deposit probably consists of their decomposed and altered remains.

Ichthoform.—A compound of ichthyol and formaldehyde; an intestinal antiseptic.

Iodol is tetra-iodopyrrol ($\text{C}_4\text{HI}_4\text{N}$); that is, it is pyrrol ($\text{C}_4\text{H}_5\text{N}$) from the molecule of which four atoms of hydrogen have been displaced by four atoms of iodine.

It is obtained by the action of iodine on pyrrol, which is an oily liquid contained in bone-oil, produced by the dry or destructive distillation of bones. Pyrrol is a ring compound having the constitutional formula—



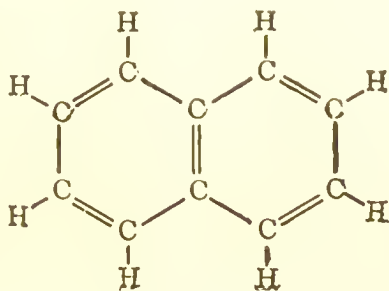
Iodol is a brownish-white powder, insoluble in water, but soluble in glycerol, alcohol, ether, and chloroform. It is used as an antiseptic.

Kryogenin (*see Cryogenin*).

Mesotan $\left\{ \begin{array}{l} \text{C}_6\text{H}_4\text{OH} \\ \text{COOCH}_2(\text{CH}_3\text{O}) \end{array} \right.$ methoxy - methyl

salicylate, used in solution in olive oil for inunction. It is a yellow liquid with a faint aromatic odour.

Naphthalene ($C_{10}H_8$).—A hydrocarbon, ob-



Naphthalene.

tained as a by-product in the preparation of coal gas; it may be regarded as two benzene rings having two carbon atoms in common. It occurs in white, shining, crystalline plates, insoluble in water, but soluble in alcohol and ether. It is an antiseptic.

β -Naphthol ($C_{10}H_7.OH$).—Two isomeric modifications, α -naphthol and β -naphthol, exist; they are derivatives of naphthalene, from the molecule of which one atom of hydrogen is displaced by hydroxyl. Naphthol occurs in white shining crystals, sparingly soluble in water, but soluble in alcohol and ether; it is a powerful antiseptic.

Phenacetine ($C_6H_4.OC_2H_5.NH.CH_3CO$). — A derivative of para nitrophenol ($C_6H_4.NO_2.OH$); crystallises in colourless, tasteless, glistening scales, melting at 135° ; not very soluble in water. An antipyretic.

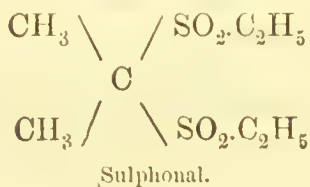
Protargal.—A silver compound of a protein, used for mucous catarrh.

Saccharin ($C_6H_4\left\{\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}\right\}NH$), *benzoyl sulphonie imide*.—This imide may be regarded as NH_3 , in which two atoms of hydrogen have been replaced

by a divalent acid radicle. Sulphobenzoic acid $C_6H_4 \begin{Bmatrix} SO_2OH \\ COOH \end{Bmatrix}$ is benzoic acid $\begin{pmatrix} C_6H_5 \\ COOH \end{pmatrix}$ in which one of the hydrogen atoms in the phenyl group is replaced by the radicle (SO_2OH) ; the imide is formed by replacing two atoms of hydrogen in ammonia by the divalent group $\begin{pmatrix} C_6H_4 \\ CO_2 \end{pmatrix}$. It is obtained by a complicated series of processes from toluene, or methylbenzene $(C_6H_5.CH_3)$. It is a white, intensely sweet powder, slightly soluble in water, more soluble in alcohol.

Salol $\begin{pmatrix} C_6H_4OH \\ COO(C_6H_5) \end{pmatrix}$, *phenyl salicylate*.—A white crystalline substance, insoluble in water, but soluble in alcohol; it possesses antiseptic and antipyretic properties.

Sulphonal is a derivative of methane (CH_4) , from the molecule of which two atoms of hydrogen are displaced by two equivalents of methyl (CH_3) , and the other two atoms by two equivalents of the ethyl sulphonic group $(C_2H_5.SO_2)$; the constitution of sulphonal is therefore diethylsulphondimethyl methane; thus—



It is produced by the oxidation of a mixture of ethyl-mercaptan and acetone. It occurs in white tabular crystals, tasteless and odourless, slightly soluble in water, and freely soluble in alcohol and ether. It is a hypnotic.

When one of the methyl groups is replaced by

ethyl (C_2H_5) the substance becomes **Trional**; when the second methyl group is also replaced by ethyl we have **Tetronal**.

Urethane $\left(\text{CO} \begin{Bmatrix} \text{NH}_2 \\ \text{OC}_2\text{H}_5 \end{Bmatrix}\right)$.—Ethyl carbamate (see page 430) occurs in colourless crystals, readily soluble in water. It is a hypnotic.

Urosin.—A compound of quinic acid and lithium, used to check gout.

Urotropine.—Aminoform or formin $[\text{N}_4\text{C}_6\text{H}_{12}$ or $\text{N}(\text{CH}_2\text{NCH}_2)_3]$ is hexamethylene tetramine. Used as an antiseptic to the urinary tract, a solvent for uric-acid concretions; should be dissolved in cold water, as boiling water decomposes it into ammonia and formaldehyde. It is prepared by evaporating a mixture of ammonia and formaldehyde, and occurs in small acicular crystals soluble in water.

Veronal $\left(\text{CO} \begin{Bmatrix} \text{NH.CO} \\ \text{NH.CO} \end{Bmatrix} \text{C}(\text{C}_2\text{H}_5)_2\right)$, *diethyl malonyl urea*.—A white crystalline powder melting at 182° . It is easily soluble in water that has been rendered slightly alkaline with caustic potash, and addition of mercuric nitrate to this solution produces a white precipitate as in the case of urea (page 532). Veronal is a soporific;

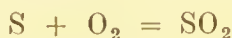
PART V.—CHEMICAL PROBLEMS

IN the earlier parts of this work some of the problems which most frequently occur have already been discussed. The conversion of a volume of gas, measured at any given temperature and pressure to the volume at N.T.P. is illustrated on page 33. The calculation of the percentage composition from the results of a quantitative analysis of a compound was explained in detail on pages 402-404. The deduction of a formula from this percentage composition is fully described on pages 414-417. In the present Part a few typical problems of a more general character, such as have actually been presented by the Examining Board to the student, will be solved.

1. What weight of sulphur would have to be burned in a room, 4 metres high, 6 metres long, and 5 metres wide, in order to convert all the oxygen in the air of the room into sulphur dioxide? The air of the room is to be taken at 20° C. and 760 mm. pressure.

$$\text{S} = 32, \text{O} = 16$$

The reaction upon which this problem is based is expressed by the equation—



This tells us that 32 grm. of sulphur combine with 22.4 litres of oxygen (measured at N.T.P.) and produce the same volume of sulphur dioxide.

$$\begin{aligned}
 \text{Vol. of air in room} &= 4 \times 6 \times 5 && \text{cubic metres at } 20^\circ \text{ and } 760 \text{ mm.} \\
 \therefore \text{,, oxygen ,,} &= 4 \times 6 && \text{cubic metres at } 20^\circ \text{ and } 760 \text{ mm.} \\
 &= 24 \times \frac{273}{293} && \text{cubic metres at N.T.P. (page 33).} \\
 &= 24 \times \frac{273}{293} \times 1000 && \text{litres at N.T.P.}
 \end{aligned}$$

but 22.4 litres of oxygen require 32 grm. of sulphur

$$\therefore 1 \text{ litre of oxygen requires } \frac{32}{22.4} \text{ ,, ,,}$$

$$\therefore 24 \times \frac{273}{293} \times 1000 \text{ litres of oxygen require}$$

$$\frac{32}{22.4} \times 24 \times \frac{273}{293} \times 1000 \text{ grm. of sulphur}$$

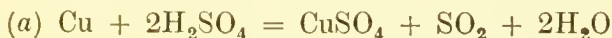
or nearly 32 kilogrammes.

2. What weight and what volume of sulphur dioxide, measured at 24° and 500 mm. pressure, will be obtained—

(a) by heating 21 grm. of copper with excess of sulphuric acid?

(b) by treating 10 grm. of sodium sulphite with excess of hydrochloric acid?

$$\text{Cu} = 63, \text{S} = 32, \text{O} = 16, \text{Na} = 23.$$



When heated as described,

63 grm. of Cu yield 64 grm. or 22.4 litres of SO_2 at N.T.P.

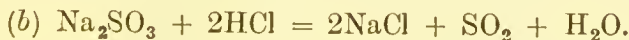
$$\therefore 21 \text{ ,, ,, } \frac{64}{3} \text{ ,, } \frac{22.4}{3} \text{ litres of } \text{SO}_2 \text{ at N.T.P.}$$

$$= 31.3 \text{ grm. or } \frac{22.4}{3} \times \frac{297}{273} \times \frac{760}{500} \text{ litres of } \text{SO}_2 \text{ at } 24^\circ \text{ and } 500 \text{ mm. (p. 33),}$$

$$= 31.3 \text{ ,, } 12.347 \text{ litres of } \text{SO}_2 \text{ at } 24^\circ \text{ and } 500 \text{ mm.}$$

Answer, 31.3 grm.

12.347 litres at 24° and 500 mm.



This example should be worked like (a).

Answer, 2.94 litres, or 5.08 grm.

3. What volume of the gaseous product, measured at 20° C. and 760 mm. pressure, will be obtained on completely decomposing by heat 10 gm. of ammonium nitrate ?

$$N = 14, O = 16.$$



This problem closely resembles the previous one, and is therefore left as an exercise for the student.

Answer, 3 litres.

4. One gm. of a metal, treated with excess of dilute sulphuric acid, yields 380 c.c. of hydrogen at 20° C. and 740 mm. Calculate the equivalent of the metal (page 48).

380 c.c. at 20° C. and 740 mm. = 345 c.c. at N.T.P. (p. 33).

Now 11.2 litres of hydrogen at N.T.P. weigh 1 gm.

\therefore 1 litre ,, ,, weighs $\frac{1}{11.2}$ "

\therefore 345 c.c. ,, ,, weigh $\frac{1}{11.2} \times \frac{345}{1000}$ "

lastly, $\frac{345}{11200}$ gm. of hydrogen is replaced by 1 gm. of metal,

\therefore 1 gm. of hydrogen is replaced by $\frac{11200}{345}$ gm. of metal,

\therefore 1 gm. of hydrogen is replaced by 32.5 gm. of metal.

Answer, 32.5.

5. The two oxides of tin contain 88.15 per cent. and 78.81 per cent. of the metal respectively. Show that the law of multiple proportions applies. (See page 50.)

The percentage composition of the two oxides is:—

Sn, 88.15,
O, 11.85.

Sn, 78.81,
O, 21.19.

\therefore in first oxide,

11.85 parts of O combine with 88.15 parts of Sn,

or $\frac{11.85}{88.15}$ " " " 1 part "

or .13443 " " " 1 " "

but in second oxide,

$\frac{21.19}{78.81}$ part of O combine with 1 part of Sn,

or .26887 " " " 1 " "

Since $\frac{.26887}{.13443}$ is practically $= \frac{2}{1}$, the law of multiple proportions is fulfilled.

6. If 0.36 gm. of an organic compound which contains only carbon, hydrogen, and oxygen, yields on combustion 0.528 gm. of carbon dioxide and 0.216 gm. of water, what is its empirical formula ?

$$C = 12, O = 16, H = 1.$$

Reference to pages 403, 415, 416 will enable the student to solve this problem.

Answer, CH_2O .

7. Fifty c.c. of a mixture of nitrous and nitric oxides were mixed with an equal volume of hydrogen in a eudiometer and the mixture was fired. After the condensation of the steam, 40 c.c. of nitrogen remained; how much nitric oxide was present ?

(For the composition of these oxides by volume, see pages 147, 150.)

Let x c.c. of nitrogen come from the N_2O
and y c.c. " " " NO

then $x + y = 40$ c.c.,

and also $x + 2y = 50$ c.c. ;

$\therefore y = 10$ c.c. ;

\therefore vol. of NO = 20 c.c.

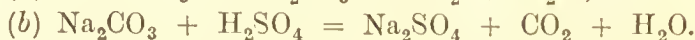
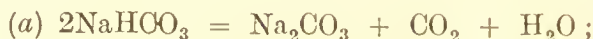
and vol. of $N_2O = 30$ c.c.

8. If a certain quantity of sodium bicarbonate is completely converted by heat into sodium carbonate,

and the carbonate thus obtained requires 24.5 grm. of a 10 per cent. solution of sulphuric acid for complete conversion to sodium sulphate, calculate the original weight of sodium bicarbonate taken and the volume of carbon dioxide, measured at 0° and 760 m.m., given off during its conversion to carbonate.

$$\text{Na} = 23, \text{C} = 12, \text{O} = 16, \text{H} = 1, \text{S} = 32.$$

The reactions are:—



The quantity of H_2SO_4 employed is 2.45 grm., and this is one-fortieth of the gram-molecule, 98. We see, therefore, that we must divide the equation weights throughout by 40.

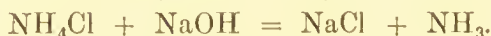
Answer, 4.2 grm. of NaHCO_3 .

56 litres of CO_2 (= 560 c.c.).

The following problems relate to volumetric analysis, and should be postponed till the student has read pages 594-99.

9. A quantity of ammonium chloride is boiled in an open vessel with 100 c.c. of normal sodium hydroxide until no further chemical change takes place; it is then found that the excess of sodium hydroxide requires 10 c.c. of normal sulphuric acid to neutralise it. How much ammonium chloride was used?

$$\text{N} = 14, \text{Cl} = 35.5, \text{H} = 1,$$



Evidently 90 c.c. of $\frac{\text{N}}{1}$ NaOH were used.

Now 1000 c.c. of $\frac{\text{N}}{1}$ NaOH react with 53.5 grm. of NH_4Cl

$$\therefore \quad 1 \quad \text{,,} \quad \text{,,} \quad \text{reacts with} \quad \frac{53.5}{1000} \quad \text{,,} \quad \text{,,}$$

$$\therefore \quad 90 \quad \text{,,} \quad \text{,,} \quad \text{react with} \quad \frac{53.5 \times 90}{1000} \quad \text{,,} \quad \text{,,}$$

$$= 4.815 \quad \text{,,} \quad \text{,,}$$

Answer, 4.815 grm.

10. (a) What weight of sodium hydroxide would be required to neutralise 100 c.c. of a normal solution of sulphuric acid?

(b) What volume of carbon dioxide measured at 15° C. and 760 mm. would be required to convert completely the above amount of sodium hydroxide into sodium bicarbonate?

$$\text{Na} = 23, \text{O} = 16, \text{H} = 1.$$

(a) To neutralise 100 c.c. of $\frac{\text{N}}{1} \text{H}_2\text{SO}_4$ requires 100 c.c. of $\frac{\text{N}}{1} \text{NaOH}$, and this contains 4 gramm. of NaOH.



To convert 40 gramm. of NaOH to NaHCO_3 requires 22.4 litres of CO_2 at N.T.P.

\therefore to convert 4 gramm. of NaOH to NaHCO_3 requires 2.24 litres of CO_2 at N.T.P.

= 2.363 litres of CO_2 at 15° and 760 mm. (page 33).

Answer, (a) 4 gramm.

(b) 2.363 litres.

11. To neutralise 10 c.c. of dilute hydrochloric acid, 40 c.c. of normal sodium hydroxide were required. In another 10 c.c. of the same acid, 1 gramm. of precipitated chalk (CaCO_3) was dissolved, and it was then found that 20.5 c.c. of normal sodium hydroxide were required to neutralise the excess of hydrochloric acid. Calculate the percentage of pure calcium carbonate in the sample of precipitated chalk.

$$\text{Ca} = 40, \text{C} = 12, \text{O} = 16.$$

We see that—

$$10 \text{ c.c. of dil. HCl} = 40 \text{ c.c. of } \frac{\text{N}}{1} \text{NaOH},$$

and also 10 c.c. of dil. HCl = 1 gramm. of chalk + 20.5 c.c.

$$\text{of } \frac{\text{N}}{1} \text{NaOH};$$

\therefore 1 gramm. of the chalk = 19.5 c.c. of $\frac{\text{N}}{1} \text{NaOH};$

but 50 gm. of pure $\text{CaCO}_3 = 1000$ c.c. of $\frac{N}{1}$ NaOH ,
 $\therefore 1$ " " " = 20 " "
 \therefore percentage of pure CaCO_3 in the sample of chalk
 is $\frac{19.5}{20} \times 100 = 97.5$.

Answer, 97.5.

12. What weight and what volume of carbon dioxide, at N.T.P., would be obtained when 1 gm. of potassium permanganate was completely reduced by oxalic acid ?

This is easily calculated from the equation on page 601.

Answer, $\frac{440}{316}$ gm.
 $\frac{224}{316}$ litres.

PART VI.—PRACTICAL CHEMISTRY

Preparation of Salts. Qualitative Analysis—Identification of Bases—Identification of Acids. Quantitative Analysis: Gravimetric Analysis: Estimation of Sulphates—Volumetric Analysis—Acidimetry and Alkalimetry—Permanganate Process—Volumetric Estimation of Chlorides and Phosphates—Weights and Measures.

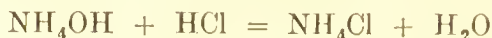
I. PREPARATION OF SALTS

THE methods most generally useful in the preparation of various substances have already been indicated in the foregoing pages. The successful application of these methods demands, however, a certain skill in manipulation which can only be acquired by actual practice in the laboratory. We shall describe in detail the preparation of a few typical compounds.*

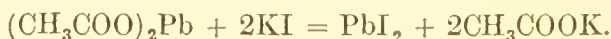
Ammonium chloride.—Place about 40 c.c. of ammonium hydrate in a porcelain basin and add hydrochloric acid until the mixture, after being stirred, is *quite neutral*—i.e. does not change the colour of either blue or red litmus paper. (The litmus paper should not be dipped into the solution, but a small drop should be taken up on the glass stirring-rod and brought into contact with the litmus paper.) Concentrate the neutral solution by evaporation on the water-bath. When it is sufficiently concentrated—as shown by the fact that the film of liquid adhering to the stirrer quickly sets

* Included by the Examining Board in the Syllabus of Practical Chemistry.

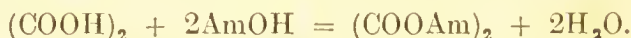
to a solid on cooling—allow the solution to cool. Drain the crystals on a porous plate.



Lead iodide.—Dissolve 5 gramm. of lead acetate or nitrate in distilled water, adding a drop or two of dilute nitric acid; then add a solution of potassium iodide as long as a precipitate falls. Filter, wash with cold distilled water, and dry on filter paper. If the precipitate be boiled with distilled water containing a little nitric acid, and the solution be allowed to cool, the lead iodide will separate out in iridescent golden spangles. The mother liquor may then be decanted and the crystals collected and dried on filter paper.



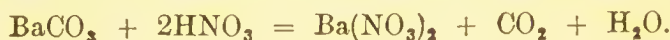
Ammonium oxalate.—Dissolve 5 gramm. of oxalic acid in 25 c.c. of hot distilled water; carefully neutralise with ammonium hydrate, and then proceed as in the preparation of ammonium chloride.



Potassium nitrate.—Dissolve 10 gramm. of caustic potash or of potassium carbonate in water; neutralise with nitric acid, evaporate to the crystallising point, and allow to cool. Decant the mother liquor and drain the crystals on a porous plate.

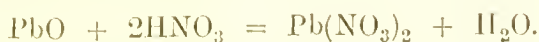


Barium nitrate.—Dissolve 10 gramm. of barium carbonate in *dilute* nitric acid with the aid of heat, boil, filter hot, evaporate to the point of crystallisation, and allow to cool. It is most important to have the solution *dilute* and *hot* while filtering, as barium nitrate is not very soluble: if the solution is strong, most of the barium nitrate will separate out and remain on the filter.



Lead nitrate.—Dissolve 10 gramm. of lead carbonate or of litharge in dilute nitric acid, with the aid

of heat; filter the solution, evaporate to the point of crystallisation, and allow to cool. Collect, and drain, the crystals as before.



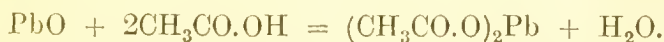
Copper sulphate.—Dissolve (in a fume cupboard) 5 grm. of copper turnings in an evaporating dish, in strong sulphuric acid; the reaction must be aided by heat. When the metallic copper has been converted into a grey powder allow the mixture to cool. Cautiously decant the excess of strong sulphuric acid and pour on the residue cold water; boil, filter, evaporate the filtrate to the crystallising point, and allow to cool. The strong sulphuric acid converts the copper into the anhydrous copper sulphate (mixed with a little sulphide). This is insoluble in the strong acid; on adding water, the grey powder dissolves to a blue solution of ordinary copper sulphate ($\text{CuSO}_4 + 5\text{H}_2\text{O}$).



Ferrous sulphate ($\text{FeSO}_4 + 7\text{H}_2\text{O}$).—To about 25 c.c. of dilute H_2SO_4 add gradually *clean* iron filings, and warm sufficiently to maintain free evolution of hydrogen. When no more iron dissolves, filter; the pale green filtrate will slowly deposit crystals; collect and drain as usual.

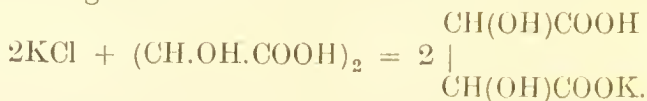


Lead acetate ($(\text{CH}_3\text{CO.O})_2\text{Pb} + 3\text{H}_2\text{O}$).—Dilute about 20 c.c. of acetic acid with an equal volume of distilled water; boil, and to the hot liquid add litharge or lead carbonate in small quantities at a time till no more dissolves. Filter, evaporate, and crystallise.

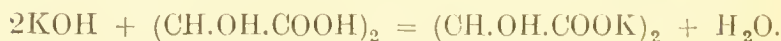


(a) Dissolve 5 grm. of potassium chloride in a small quantity of water, and 6 grm. of tartaric acid also in a

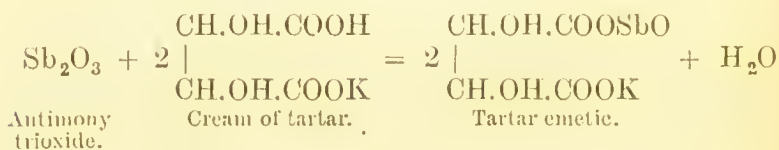
small quantity of water, mix the solutions and allow to stand; filter off the white precipitate and recrystallise from boiling water.



(b) Dissolve 5 gm. of tartaric acid in water, divide the solution into two equal parts, *neutralise* one carefully with KOH, then mix it with the rest of the tartaric acid, allow to stand, filter and recrystallise from hot water.



Tartar emetic.—Boil 5 gm. of antimony oxide. 7 gm. of cream of tartar, and 40 c.c. of water for ten minutes, filter through a funnel and filter paper, previously warmed by pouring through them boiling water, and allow to crystallise.



II. QUALITATIVE ANALYSIS

It has already been stated (pages 105, 106) that salts are ionised in solution, and that the analytical reactions by which they are identified are really due to the ions.

Our “tests” are therefore tests for ions. They may be divided into: (1) tests for positive ions or kations, and (2) tests for negative ions or anions. Metallic salts result, as we have seen, from the reaction between a base and an acid (page 65). When we have identified the positive ion, we know the

base, and when we have identified the negative ion we know the acid. If, for instance, in an aqueous solution of silver nitrate we have identified the silver ion (Ag^+) and the nitrate ion (NO_3^-), then we know both the base (AgOH) and the acid (HNO_3) from which the given salt may be derived; the two partners are sometimes distinguished as the metallic radicle (Ag) and the acid radicle (NO_3). The result of our analysis might therefore be stated as—

	Found,	positive ion	Ag^+
		negative ion	NO_3^-
or,	Found,	base	AgOH
		acid	HNO_3
or,	Found,	metallie radicle	Ag
		acid radicle	NO_3

The analysis of a single salt in aqueous solution is probably the simplest exercise of the kind which is likely to be presented to the student, and it may often be accomplished by methods which would be quite unsuited to more complex analyses. The presence of two or more salts in the same solution necessitates more careful and thoughtful work, and exercises of this type are therefore more generally set at the present time. The analysis of solid substances (1) insoluble in water, and (2) insoluble in acids, may be said to mark further stages of increasing difficulty in our task. All these cases, however, have certain general features in common, and these will now be described.

The analysis is divided into two parts:

- (1) The identification of the bases.
- (2) The identification of the acids.

For (1) we require a suitable solution containing the bases. In this solution the bases need not be combined with their original acids, but may be combined instead with any other acid. This solution is obtained by methods described on pages 580-82, and is then analysed for the bases by the scheme on pages 583-87.

For (2) we require a suitable solution containing the acids. In this solution the acids need not be combined with their original bases, but may be combined, instead, with any other base. They are usually present as sodium or potassium salts. This solution is obtained by methods described on pages 587 and 588, and is analysed for the acids by the scheme on pages 588-92.

Preparation of the solution for the identification of the bases (with special reference to the requirements of candidates for the First Professional, or First M.B., Examination).

If the substance offered for analysis is, or can be, dissolved in water this aqueous solution requires no further preparation, and can be at once examined by the scheme set out on pages 583-87.

If only a portion is soluble in water, this portion should be separated and examined as above.

If insoluble in water the substance should now be tested to ascertain whether it is, or is not, one of the following three salts: a phosphate (*see* page 228, test 3), an oxalate (*see* page 510, test 2), a tartrate (*see* page 514, test 3). The answer to this question influences our subsequent process.

No phosphate, oxalate, or tartrate is present.—We now try to dissolve the substance in hot water by the gradual addition of hydrochloric acid, or nitric acid, or both, to the water. If it is still insoluble, the same treatment is applied to the solid, without water. A solution effected in this way is often unsuitable for immediate examination by the scheme, owing to the

presence of much free nitric acid or aqua regia. This free acid may be removed by boiling down the solution (in a fume cupboard) to near dryness, and taking up the residue in hot distilled water. The solution will now contain the bases as chlorides* or nitrates, and can be examined by the scheme (pages 583-87).

The solid is a phosphate, oxalate, or tartrate.—In this case we may adopt (1) a particular or (2) a general, method. Arguments might be advanced for either course; both will be described.

1. *Special method for oxalate or tartrate.*—Heat the solid strongly on a piece of porcelain, or platinum† foil; dissolve the residue (which is an oxide or carbonate of the base) in acid, and examine this solution by the scheme (pages 583-87).

Special method for phosphate. — (a) *The phosphate dissolves in water on addition of acetic acid.* To this solution add a few crystals of sodium acetate and then ferric chloride drop by drop, till a permanent deep-red colour shows that all the phosphate has been precipitated as a yellowish-white precipitate, and soluble ferric acetate is beginning to appear. Filter and boil the red filtrate to precipitate the excess of iron as the brownish-red, basic acetate. Filter again to obtain a clear, iron-free filtrate containing the chloride of the base, which can now be examined by the scheme (pages 583-87).

(b) *The phosphate does not dissolve in water on addition of acetic acid*, but does so on addition of a little hydrochloric or nitric acid. Test this solution as usual for bases in Group I. or II. If none is found, or if more remain to be found, treat the solid by the following general method:

2. *General method for phosphate, oxalate, tartrate, or other salts insoluble in water.*

Mix about 2 gram. of the solid with three or four times its weight of dry sodium carbonate, place the mixture in a porcelain dish, cover well with distilled water, and boil the mixture for ten minutes, with constant stirring.

* Silver ehloride, if present, separates from the solution and is easily identified.

† See Caution on page 582.

Filter, taking care to transfer all the undissolved substance to the filter paper. Wash it well with hot water, and finally dissolve in dilute acid and test this solution for the base by the usual scheme. It is convenient to select for solution in this case, if possible, an acid which dissolves the newly formed carbonate of the base, but would not dissolve any undecomposed phosphate, etc., from the original solid. Thus acetic acid might be used with advantage in the case of oxalates and phosphates insoluble in this acid, and dilute nitric acid, instead of hydrochloric, in cases where there was reason to suppose that the base belonged to Group I.

This general method is rendered even more effective by substituting fusion mixture for sodium carbonate, and fusion on platinum foil for digestion in the porcelain dish. This modification easily yields satisfactory results, even with such an intractable substance as barium sulphate. After fusion, the mass is well boiled with water, filtered, and then treated as before.

We have thus obtained in every case a solution which may be analysed for bases by the scheme on pages 583-87.

It is, however, often possible to identify constituents of a substance without bringing it into solution, by what are called "dry" tests. The following are useful ones and the first should always be performed before heating the substance on platinum; if easily fusible metals, like lead, are present, they may alloy with the platinum and perforate it.

DRY TESTS (FOR BASES)

Make an intimate mixture of the dry solid with dry sodium carbonate and fine charcoal by grinding these substances together in a small mortar.

1. Heat a portion of the mixture on charcoal with the reducing flame of the blowpipe.

A bright, metallic bead is obtained, which is

Soft, malleable, and marks paper	= Pb
Not soft, but malleable	= Ag or Sn
Hard and brittle	= Bi or Sb

Remove the bead and warm with HNO_3 in test tube:

(a) It dissolves = Pb, Ag, or Bi.

Test the solution by the scheme (page 584).

(b) A white powder is obtained = Sb or Sn.

Dissolve in HCl and test as usual (Table II., p. 585):

No bead is obtained, but

Red scales = Cu.

Dissolve in HNO_3 and test as usual (page 383).

2. Heat a portion of the mixture in a glass tube:

Sublimate of metallic globules = Hg

Black mirror + garlic odour = As.

3. If the residue in the tube, or the fused mass on charcoal, be boiled with distilled water and the solution filtered, the alkaline filtrate can be used for the detection of sulphur, which will now be present as alkaline sulphide and will therefore cause—

(a) A brown colour when added to a drop of lead acetate on a white dish.

(b) A black stain on a silver coin.

4. Other dry tests depend on the colour given to a borax bead by a metallic oxide, or on the colour given to a non-luminous flame by a volatile metallic compound—e.g. the chloride. These tests are chiefly useful in the analysis of single substances, and examples of their application will be found in the course of the scheme.

ANALYSIS OF THE SOLUTION FOR BASES

1. Note carefully any obvious features of the solution, such as:—

(a) Colour—e.g. Fe''' , Cu'' .

(b) Odour. Also warm a portion with caustic potash, and note whether ammonia is evolved, proving presence of *one* base—**ammonium**.

(c) Reaction to litmus. Alkaline reaction would indicate one of the following: Ba, Sr, Ca, Mg, Na, K, NH_4 . Acid reaction: aqueous solutions of many metallic salts have a slight acid reaction (ionic), but a marked acid

reaction due to free acid other than HCl should be very nearly neutralised by addition of ammonia solution, drop by drop, before proceeding to 2.

2. To the solution add HCl and filter (if necessary)

ppt. I.
Examine by
Table I., page
585.

Filtrate.
Pass H_2S to saturation and
filter (repeat if necessary)

ppt. II.
Examine by
Table II., page
585.

Filtrate.
Boil off H_2S ; add drop or two
of strong HNO_3 ; concentrate,
filter again, and to this filtrate
add equal volume of AmCl. Aq.
and excess of $\text{NH}_3\text{. Aq.}$ and
filter

ppt. III.
Examine by
Table III., page 586.

Filtrate.
Saturate with H_2S (alkaline)
and filter

ppt. IV.
Examine by
Table IV., page 586.

Filtrate.
Add $\text{Am}_2\text{CO}_3\text{. Aq.}$
Warm, wait, and
filter

ppt. V.
Examine by
Table V., page 587.

Filtrate.
Add $\text{Na}_2\text{HPO}_4\text{. Aq.}$
Warm, shake, and wait.
White ppt., MgNH_4PO_4
= **Mg.**

To test for **K** and **Na**, boil a portion of the *original aqueous* solution with $\text{Am}_2\text{CO}_3\text{. Aq.}$ filter, and evaporate the filtrate to dryness. Transfer the dry residue to Pt foil and heat it strongly. Moisten it, after ignition, with strong HCl , and heat it in the Bunsen flame on a clean platinum wire.

The flame is coloured violet = **K**,
" " " golden yellow = **Na**.

TABLE I

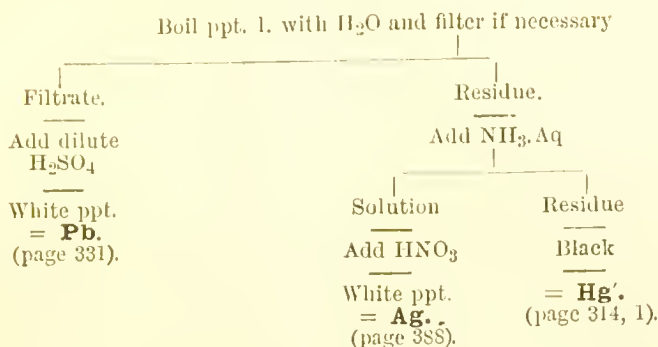


TABLE II

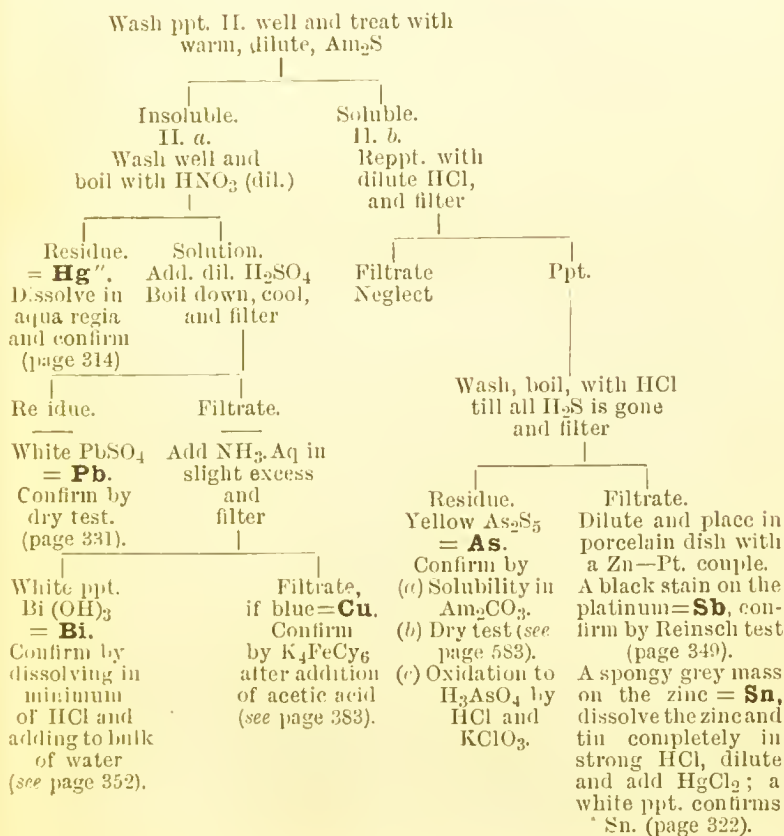


TABLE III*

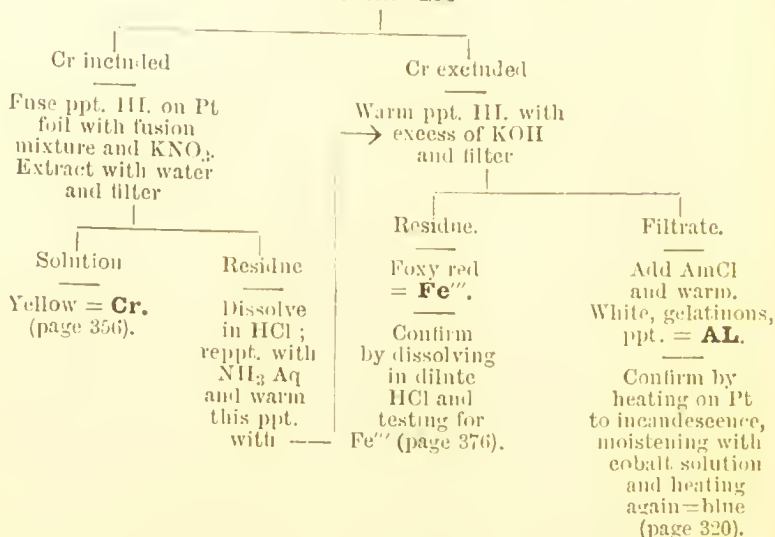
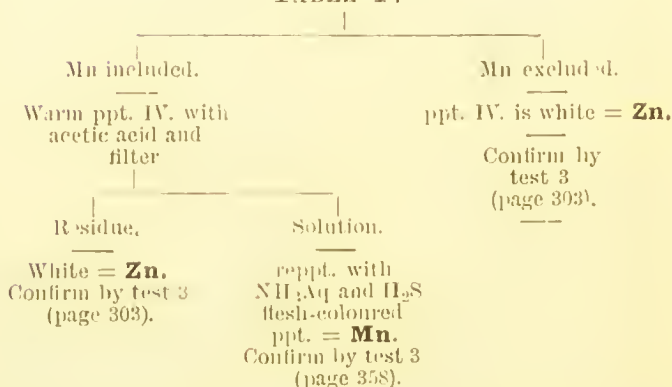
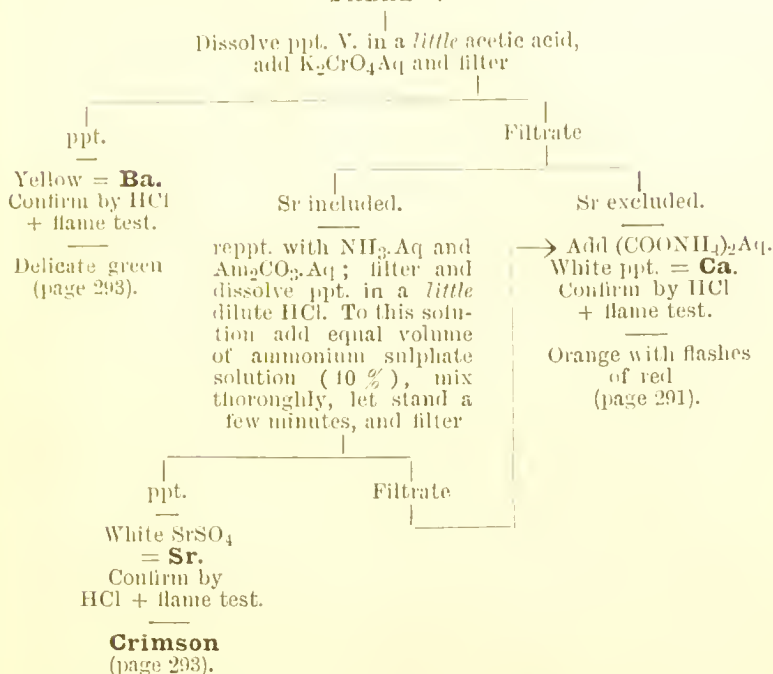


TABLE IV



* N.B.—If the solution analysed is neither an aqueous solution nor a solution prepared as directed on page 580, ppt. III. may contain a phosphate, oxalate, or tartrate, insoluble in water. In this case, therefore, the ppt. must be tested for these three salts, and if any one of them is found, reference should be made to page 581 and the suitable procedure followed accordingly.

TABLE V



Preparation of the solution for the identification of the acids (with special reference to the requirements of candidates for the First Professional or the First M.B. Examination).

If no base is present except Na, K, or NH_4 , an aqueous solution of the substance can be obtained and can be examined, without further preparation, by the scheme on page 588.

If any other base has been found, proceed as follows:—Boil some of the solid, or solution, originally given for analysis, with Na_2CO_3 Aq as in (2), page 581. Filter, and divide the clear, alkaline filtrate into three portions. Acidulate one portion (A) with dilute HNO_3 , boil off CO_2 , and finally neutralise with NH_3 Aq; A may now be tested for every acid except HNO_3 by the scheme on pages 585-92. Acidulate a second portion (B) with dilute H_2SO_4 , boil off CO_2 , and finally neutralise with NH_3 Aq; B may now be tested for HNO_3 and, if required,

for any other acid except H_2SO_4 . The third portion (C) is not acidulated at all, and a small quantity of it may be used to test for a *sulphide* by the tests (a) and (b) in (3) page 583). It is conducted by the scheme on page 589.

It is, however, often possible (as with bases) to identify the acid radicle of a salt by experiments with the dry solid, especially by observing the result of the action of HCl and of H_2SO_4 upon the salt. Useful information is so often obtained in this way that some of the solution should be evaporated to dryness to obtain a little solid for the purpose, if necessary. This examination should, however, in general be regarded as preliminary to, and not as a substitute for, the systematic examination in the wet way.

EXAMINATION OF SOLUTION A (PAGE 587), OR OTHER SUITABLE SOLUTION, FOR THE ACIDS.

1. To a small portion of the neutral solution in a test-tube add BaCl_2Aq . If a ppt. is obtained, examine it by Table 1, and then proceed to 2. If no ppt. is obtained, proceed at once to 2 (page 590).

TABLE 1

Colour of ppt.	Soluble in Acetic Acid.	Insoluble in Acetic Acid	
		Soluble in dilute HNO_3 .	Insoluble in dilute HNO_3 .
White	Arsenite Borate* Carbonate (with effervescence) Hydroxide Phosphate Tartrate (from strong solutions only)	Oxalate Sulphite* (SO_2 evolved) Sulphocyanide*	Sulphate Fluo-silicate*
Yellow		Chromate*	

* Not included in Syllabus of Examining Board.

PRELIMINARY EXAMINATION FOR AN ACID

I. Add a little of the solid to some dilute HCl in a test-tube and warm

H ₂ evolved.	CO ₂ evolved.	H ₂ S evolved.	SO ₂ evolved.	Oxides of N ₂ evolved.	Odour of hydrocyanic Acid (very poisonous).	Odour of Acetic Acid.	Yellow Gas, with Cl-like smell (Euchlorine).
Metallic element.	Carbonate or bicarbonate.	Sulphide.	Sulphite or Thiosulphate.	Nitrite.	Cyanide.	Acetate.	Chlorate.*

II. Add a little of the solid to some strong H₂SO₄ in a test-tube and heat

Colourless fuming vapours of HCl.	Brown choking fumes of Br.	Brownish-red Fumes of Oxides of Nitrogen.	Violet vapours of Iodine.	Chars, evolves CO and CO ₂ , and leaves odour of burnt sugar.	Effervesces when hot. CO and CO ₂ evolved.	Odour of strong Vinegar	Yellow gas, with Cl-like smell, which detonates on heating.
Chloride.	Bromide.	Nitrate or Nitrite.	Iodide.	Tartrate.	Oxalate.	Acetate.	Chlorate.*

* CAUTION.—Use *very little* solid in II. if chlorate is detected in I. This salt is not included in the Syllabus of the Examining Board.

2. To a small portion of the neutral solution in a test-tube add $\text{AgNO}_3\text{.Aq.}$ If a ppt. is obtained, examine it by Table 2, and then proceed to 3. If no ppt. is obtained, proceed at once to 3.

TABLE 2.

Colour of ppt.	Soluble in dilute HNO_3		Insoluble in dilute HNO_3	
	Soluble in $\text{NH}_3\text{.Aq.}$	Insoluble in $\text{NH}_3\text{.Aq.}$	Soluble in $\text{NH}_3\text{.Aq.}$	Insoluble in $\text{NH}_3\text{.Aq.}$
White or nearly white.	* Borate (ppt. turns brown when heated) (page 219). Oxalate (page 510). Tartrate (only from strong solutions) (page 514).	Carbonate (nearly).	(2) { Bromide (with difficulty). Chloride. Cyanide. * Ferrocyanide (with difficulty). * Sulphocyanide (*Thiosulphate, see page 256).	
Yellow	(1) { Arsenite. Phosphate.			Iodide (3).
Red, or nearly red.	Arsenate. * Chromate (page 356).		* Ferrieyanide.	
Black		Sulphide.		
Brown	Hydroxide.			

* Not included in Syllabus of Examining Board.

(1) To distinguish, see 5 (a), page 591.

(2) To distinguish, see 5 (b), page 591.

(3) For confirmatory tests, see page 193.

3. To a small portion of the neutral solution add two or three drops of $\text{FeCl}_3\text{.Aq.}$ If the colour of the solution shows any marked change, refer to Table 3. If no such change is observed, proceed at once to 4.

TABLE 3

The colour of the solution changes to		For confirmatory tests, see
Red.	Acetate.	Page 499.
Blood Red.	Sulphocyanide.	Page 525.
" . "	Meeonate.	Page 557.
Olive Green.	Ferricyanide.	Page 524.
Deep Blue (with ppt.).	Ferrocyanide.	Page 518.

4. If an acid still remains to be found, the salt is probably one of the following :—

Tartrate (in somewhat dilute solution).—If this was indicated in preliminary analysis II., page 589, we can confirm now by adding $\text{CaCl}_2 \cdot \text{Aq}$ to the neutral solution A, shaking, and warming. A white ppt. should be obtained, which should give the same dry test for tartrate.

Nitrate.—Test solution B, page 587, as described on page 156.

* *Nitrite*.—Test solution C, page 588, as described on page 159.

* *Chlorate*.—Sufficiently indicated in preliminary analysis.

* *Thiosulphate*.—Test solution C, page 588, as described on page 255.

5. (a) *Distinction between arsenite and phosphate*.—Add dilute HCl to a portion of A or B, page 587, and pass H_2S ; a yellow ppt. indicates an arsenite.

(b) *Distinction between Chloride, Bromide, and Cyanide*.—Test a portion of A or B for cyanide by the special test described on page 523. Distinguish bromide from

* Not included in Syllabus of Examining Board.

chloride by (1) the difficulty of solution in ammonia and (2) the special test for bromide on page 188.

6. Two special cases remain to be briefly considered :—

(a) The metal may be present as *element*. This is usually detected by examining it with a pocket lens, and by observing the effect on it of the action of acids (page 74).

(b) The metal may be present as *oxide*. If this is suspected from the failure to find an acid, confirmation may generally be obtained from one or more of the following experiments and observations :—

i. Mix the suspected oxide with fine carbon, and heat the mixture in a test-tube; with many metallic oxides CO_2 is evolved (page 200).

ii. Place a few grains of the sample on separate blue and red litmus papers; moisten the grains with a drop of distilled water, and observe after a few moments. A blue mark will appear on the red paper if the substance is an oxide of Na, K, Ba, Sr, Ca, or Mg; a red mark will appear on the blue paper if the substance is an oxide of arsenic.

iii. Compare the colour of the specimen with that ascribed to the suspected oxide in the text. The oxides which respond to test ii. are all white, or nearly so; many of those which respond to test i. are coloured, including: Ag_2O , Hg_2O , CuO , Fe_3O_4 , black or nearly so; PbO , Pb_3O_4 , HgO , Cu_2O , Fe_3O_3 , red or nearly so; PbO_2 , brown; Sb_2O_3 , Bi_2O_3 , cream-yellow. SnO_2 is white, and is reduced with difficulty.

ZnO and Al_2O_3 respond to neither test. Both are white when cold and are easily identified by the dry tests (pages 303, 320).

III. QUANTITATIVE ANALYSIS

When a substance has been identified the qualitative analysis is complete; if, however, we desire to know to what extent the substance identified is present in the mass examined, a quantitative analysis must be performed. This is always effected by one

of two methods—(1) gravimetric analysis, (2) volumetric analysis.

GRAVIMETRIC ANALYSIS

In this method a constituent is usually estimated by separating it, in some known form, from the solution (or solid) examined and actually weighing it, after separation has been effected. It is clear that to obtain an accurate result (1) the separation must be as complete as possible and (2) the form in which the constituent is separated should be one which can be washed, dried, etc., without undergoing indefinite alteration. Both conditions are sufficiently fulfilled in the usual gravimetric method for the estimation of sulphates, which will now be described in some detail.

GRAVIMETRIC ESTIMATION OF SULPHATES

(1) A few drops of HCl are added to a measured volume of the sulphate solution, contained in a lipped beaker; (2) the solution is then heated to the boiling point; (3) the source of heat is removed, and BaCl_2Aq (saturated) is added to the hot solution, in small quantities at a time; (4) the white ppt. of BaSO_4 is allowed at times to settle down, leaving the supernatant liquid clear enough to observe whether a drop of the reagent now produces any further ppt.; (5) when no more BaSO_4 comes down the beaker is set aside, *if time allows*; (6) the ppt. is afterwards transferred to a filter and washed *till the washings are free from Cl*; (7) the washed ppt. must now be dried on its filter in the water oven; (8) the dried ppt., detached from the filter paper, is placed in a weighed platinum (or porcelain) crucible; the filter paper is separately burnt, and its ash added to the ppt.; (9) the whole is then ignited and directly after ignition the crucible, with its contents, is placed in the desiccator to cool, and is finally weighed when cold. After deducting the weight of the crucible, we obtain the weight of BaSO_4 ,

and this, when multiplied by $\frac{96}{233}$, will give the weight of SO_4 , present as sulphate in the measured volume of solution employed.

VOLUMETRIC ANALYSIS

Gravimetric estimations obviously consume a large amount of time, as the washing and drying of the precipitate to be weighed is a protracted process. The volumetric method dispenses with these tedious operations and therefore enables us to obtain an estimation with far greater rapidity. The method necessitates the employment of "standard solutions"—that is to say, solutions of a certain known strength. The student has already learned that when two substances react chemically they do so in certain proportions by weight, which, though not equal, are *equivalent*. If these two equivalent weights were separately dissolved in distilled water, and the two solutions were carefully made up to the same volume—say 1 litre, then clearly the whole of one solution would exactly react with the whole of the other. Also any *volume* of the one would exactly react with the *same* volume of the other. This is really the foundation of the method.

The standard solution can be made of any strength, but a *certain* strength is found to be the most convenient standard for ordinary work; this is the *normal* solution.

A normal solution contains the hydrogen equivalent of the active substance in grammes per litre or 1,000 c.c.

Thus normal HCl , usually written $\frac{\text{N}}{1}\text{HCl}$, contains $1 + 35.5 = 36.5$ gram. of HCl per litre.

$\frac{\text{N}}{1}\text{HNO}_3$, $1 + 14 + 48 = 63$ gram. of HNO_3 per litre.

$\frac{\text{N}}{1}(\text{COOH})_2\text{H}_2\text{O}$, $\frac{24 + 64 + 2 + 36}{2} = 63$ gram. of oxalic acid per litre.

$$\frac{N}{1} \text{H}_2\text{SO}_4, \frac{2 + 32 + 64}{2} = 49 \text{ gm. of H}_2\text{SO}_4 \text{ per litre.}$$

It will be noticed that the molecular weights of the dibasic acids, oxalic and sulphuric, are divided by 2 so as to obtain the weights which contain one of replaceable hydrogen.

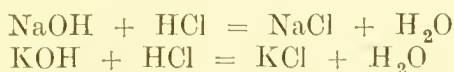
$$\frac{N}{1} \text{NaOH}, 23 + 1 + 16 = 40 \text{ gm. of NaOH per litre.}$$

$$\frac{N}{1} \text{KOH}, 39 + 1 + 16 = 56 \text{ gm. of KOH per litre.}$$

$$\frac{N}{1} \text{Ba(OH)}_2, \frac{137 + 2 + 32}{2} = 85.5 \text{ gm. of Ba(OH)}_2 \text{ per litre.}$$

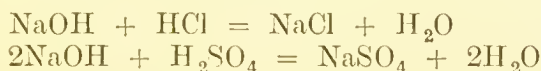
Very often the normal solution is too strong and $\frac{N}{10}$ a decinormal, or $\frac{N}{100}$ centinormal, solution is employed instead.

The great advantage of normal solutions of acids and alkalies is that a litre of any or all of them has exactly the same neutralising power, thus:



i.e. 40 gm. of NaOH neutralise the same weight of HCl as 56 gm. of KOH, and these are the respective quantities contained in a litre of $\frac{N}{1}$ NaHO and $\frac{N}{1}$ KHO, so that any volume of normal soda neutralises the same quantity of acid as the same volume of normal potash.

The same holds good with the acids, thus:



i.e. 36.5 gm. of HCl neutralise 40 gm. of NaOH, and 98 gm. of H_2SO_4 neutralise 80 gm. of NaOH, or 49 gm. of H_2SO_4 neutralise 40 gm. of NaOH. So a

litre of $\frac{N}{1} \text{H}_2\text{SO}_4$ neutralises the same weight of NaOH as a litre of $\frac{N}{1} \text{HCl}$.

In order to make accurate estimations by volumetric analysis we require :

1. Accurately graduated vessels.
2. Accurate standard solutions.
3. Reactions of which the "end-point" is sharp and easily recognised by the eye.

The various volumetric processes may be divided into three main groups.

1. Acidimetry and alkalimetry. In these processes one substance neutralises another of opposite properties.

2. Processes involving oxidation and reduction. The potassium permanganate process (page 599) is a favourite example of these.

3. Processes involving precipitation. These are illustrated by the estimation of chlorides (page 602) and of phosphates (page 603).

A measured sample of the solution, the strength of which has to be determined, is conveniently delivered from a "pipette" into a dish, beaker, or small flask; the standard solution is delivered from a vertical glass tube of uniform bore called a "burette," which usually contains 50 c.c. and is graduated to $\frac{1}{10}$ of a c.c.; it is furnished at its lower end with some kind of tap. The *lower* meniscus of the fluid surface is usually read, and the eye must be *level* with the meniscus when reading. The burette, after thorough washing with distilled water, should always be rinsed out with a small quantity of the standard solution, and the air bubble in the tap washed out before reading; the graduation at which the meniscus stands *should always be written down* before commencing the analysis.

ACIDIMETRY AND ALKALIMETRY

1. Estimation of the strength of a solution of KOH or NaOH by standard acid.

For these estimations $\frac{N}{1}$ or $\frac{N}{10}$ acid is employed in the laboratory, but in examinations an acid of any strength may be given; in any case the strength must be known,

and will be most conveniently expressed as *some fraction of normal*.

10, 20, or 50 c.c. of the solution are measured off in a pipette or measuring flask, and placed in a flask or beaker; some substance termed an "indicator" is then added, which indicates by its change of colour whether the solution is alkaline or acid; it is also advisable to dilute the solution with distilled water. The indicators most frequently employed are:—

Litmus, blue with alkalis, red with acids.

Phenolphthalein, pink with alkalis, colourless with acids.

Methylorange, yellow with alkalis, red with acids. Litmus is not good when artificial light is used. Phenolphthalein is used only with strong bases—e.g. NaOH and KOH, and especially for titrating organic acids—e.g. oxalic acid. Methylorange is sensitive even to weak bases—e.g. $\text{NH}_3\text{.Aq}$ —but is not sensitive to weak acids—e.g. carbonic acid. It is, therefore, mainly used with mineral acids (HCl , H_2SO_4 , HNO_3), especially for titrating alkaline carbonates.

The standard acid is added carefully till the "indicator" denotes that the solution is just acid. It saves time, if two quantities of the solution can be obtained, to run in the standard acid in quantities of 1 c.c. at a time, so as to get a rough idea of how much acid is required, and then to repeat the experiment, running in $\frac{1}{10}$ of a c.c. towards the end of the experiment, thus:

Suppose 25 c.c. of the acid failed to turn the colour of the indicator, but 26 c.c. very obviously too much, the experiment is repeated with a similar sample of the solution, 24.5 c.c. of the acid are run in and then 2 drops ($= \frac{1}{10}$ c.c.) added, at a time, until the colour changes. Two estimations, at least, must always be made, and if these do not agree very closely a third must be made. The mean result is finally adopted.

Suppose the problem was, "To find the strength per litre of a solution of KOH, $\frac{N}{1}$ acid being given." As the acid is of "normal" strength the *nature* of the acid, whether HCl , H_2SO_4 , etc., makes no difference; 25 c.c.

of the KOH solution are taken, and one or two drops of an alcoholic solution of phenolphthalein added, the solution turning pink.

28 c.c. of acid failed to destroy the pink colour, but 29 c.c. rendered the fluid colourless.

The experiment is repeated with a second portion of 25 c.c. 28 c.c. of the acid are run in at once, and then two drops at a time ; the colour goes at 28.3 c.c.

Since 28.3 c.c. of the $\frac{N}{1}$ acid neutralise only 25 c.c. of the KOH solution, the KOH solution must be the stronger, and it must be $\frac{28.3}{25} \times \frac{N}{1}$ KOH. It must therefore contain $\frac{28.3}{25} \times 56 (=63.4)$ gram. of KOH per litre.

A similar procedure is adopted with the other acids and bases.

To take another example. "Find the strength of a solution of nitric acid, and calculate the amount of water to be added to it to bring it to $\frac{N}{1}$ strength, $\frac{N}{1}$ NaOH being provided."

25 c.c. of the nitric acid are taken, phenolphthalein is added as before, and the $\frac{N}{1}$ NaOH run in from the burette ; when 30 c.c. have been added the solution is still colourless, but at 31 c.c. it is pink. Repeating the experiment with a second quantity of 25 c.c., the colour changes at 30.6 c.c.

Since 30.6 c.c. $\frac{N}{1}$ NaOH neutralise only 25 c.c. of the HNO_3 solution,

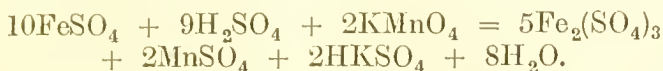
\therefore this HNO_3 solution must be $\frac{30.6}{25} \times \frac{N}{1} \text{HNO}_3$ and must contain $\frac{30.6}{25} \times 63$ gram. of HNO_3 per litre = 77.112 gram. of HNO_3 per litre.

To reduce this to $\frac{N}{1} \text{HNO}_3$ we must take $\frac{25}{30.6}$ of a litre of this acid and dilute it with distilled water to 1 litre.

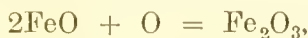
OXIDATION BY KMnO_4

The process of oxidation by a solution of potassium permanganate can be, at first, most profitably studied with the ferrous salts.

The reaction is represented by the equation :



It will be seen that in the above equation 10 atoms of iron are oxidised to the ferrie state by 2 molecules of potassium permanganate, or 1 molecule of KMnO_4 oxidises 5 atoms of Fe'' to Fe''' ; now, 2 atoms of iron in the ferrous state require 1 atom of oxygen to convert them into the ferrie condition, thus



and 1 atom of oxygen can also oxidise 2 atoms of hydrogen to H_2O .

So that, as far as the above reaction is concerned, 1 atom of O which oxidises 2 atoms of Fe'' to Fe''' is equivalent to 2 atoms of H.

\therefore the available oxygen in 1 molecule of KMnO_4 is equivalent to 5 atoms of H, and the weight of KMnO_4

required to form a $\frac{\text{N}}{1}$ solution of KMnO_4 is one-fifth of its molecular weight = $\frac{39 + 55 + 64}{5} = 31.6$ gm.

So $\frac{\text{N}}{1}$ solution of KMnO_4 contains 31.6 gm. in the litre.

Ordinary ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is apt to oxidise on keeping, so the ferrous ammonium sulphate $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, which keeps well, is preferable. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O} = 56 + 32 + 64 + 36 + 32 + 64 + 108 = 392$; so 392 gm. of the sulphate contain 56 gm. of Fe. It is convenient, therefore, to remember that any weight of this salt contains exactly one-seventh of its weight of ferrous iron.

Suppose the strength of a KMnO_4 solution is to be determined :

0.7 gram. of the above salt (after powdering and pressing between filter paper) is weighed out and dissolved in about 200 c.c. of distilled water which has been previously boiled, to free it from air, and acidulated with H_2SO_4 .

The KMnO_4 is run in from a burette, as before, until the solution turns pink—i.e. until all the iron has been oxidised and the KMnO_4 is no longer decolorised.

Suppose 18 c.c. are required to produce a pink colour : Since .7 gram. of the salt contains 0.1 Fe'' and has been dissolved in 200 c.c. of solution,

\therefore 1 litre of this ferrous solution would contain .5 gram. of Fe'' ;

but 1 litre of $\frac{\text{N}}{10}$ ferrous solution contains 5.6 grms. of Fe'' ;

\therefore this ferrous solution is $\frac{.5}{5.6} \times \frac{\text{N}}{10}$;

\therefore the KMnO_4 solution must be $\frac{200}{18} \times \frac{.5}{5.6} \times \frac{\text{N}}{10}$
 $\left(= \frac{100}{100.8} \times \frac{\text{N}}{10} \right)$.

If the strength of the KMnO_4 solution is known, it can be used to determine the amount of iron in any substance containing that metal, but the iron must be in the *ferrous* state ; if it is present as ferrie iron it must be reduced by nascent hydrogen (zinc and sulphuric acid) or by passing SO_2 gas, etc., until the solution is colourless.

As an example 0.5 gram. of an iron ore was dissolved, the solution reduced with zinc, the excess of zinc removed, the solution required 42 c.c. of $\frac{\text{N}}{10} \text{KMnO}_4$ to turn it pink.

1 c.c. of $\frac{\text{N}}{10} \text{KMnO}_4$ oxidises .0056 gram. Fe

\therefore 42 c.c. of $\frac{\text{N}}{10} \text{KMnO}_4$ oxidise .2352 gram. Fe.

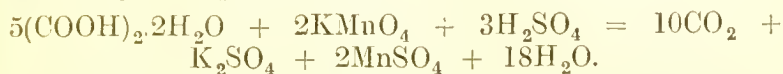
So the ore contained in 100 parts, $\frac{.2352 \times 100}{.5} = 47.04$ per cent. Fe.

KMnO_4 solution has the disadvantage that it cannot

be used in the presence of HCl; it is also reduced by organic matter.

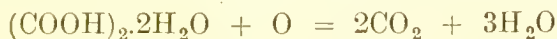
ACTION OF POTASSIUM PERMANGANATE ON OXALIC ACID

The reaction between KMnO_4 and $(\text{CO.OH})_2$ is represented by the equation



Two molecules of KMnO_4 oxidise 5 molecules of oxalic acid, which crystallises with 2 molecules of water.

Two molecules of KMnO_4 contribute 5 atoms of available oxygen (*see* oxidation of Fe by KMnO_4 , page 599). So 16 grm. of oxygen oxidise 1 grm.-molecule of oxalic acid.



and $\frac{\text{N}}{1}$ oxalic acid, i.e. $\frac{126}{2} = 63$ grm. to the litre, will be exactly oxidised by an equal volume of $\frac{\text{N}}{1}$ permanganate, containing 31.6 grm. in the litre, because 31.6 grm. of KMnO_4 evolve 8 grm. of oxygen, which oxidise half a grm.-molecule or 63 grm. of oxalic acid, as seen in the equation above.

As an example, take the following problem:—Find the strength of a solution of oxalic acid, $\frac{\text{N}}{1}\text{KMnO}_4$ being given.

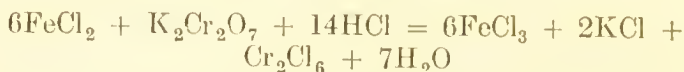
50 c.c. of the oxalic acid solution is taken, acidified with sulphuric acid, and heated to about 60°C . (as the reaction does not start at once in the cold); $\frac{\text{N}}{1}\text{KMnO}_4$ is then added till the fluid is just pink.

Suppose 45 c.c. of the $\frac{\text{N}}{1}\text{KMnO}_4$ are required; then

the oxalic acid solution must be $\frac{45}{50} \times \frac{\text{N}}{1}$,

and \therefore must contain $\frac{45}{50} \times 63$ grm. of $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ per litre = 56.7 grm. of $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ per litre.

For some purposes a solution of potassium bichromate is preferable to a solution of potassium permanganate, since it is not affected by the presence of hydrochloric acid or organic matter. The reaction is



1 molecule of $\text{K}_2\text{Cr}_2\text{O}_7$ oxidises 6 atoms of Fe.

So $\frac{\text{N}}{1} \text{K}_2\text{Cr}_2\text{O}_7$ contains $\frac{78 + 104.8 + 112}{6} = 49.13$ gm. in 1000 c.c.

There is no marked change of colour when the iron is completely oxidised with HCl and $\text{K}_2\text{Cr}_2\text{O}_7$, so that the solution is tested for the presence of a ferrous salt by withdrawing from time to time small drops of the liquid and mixing them on a white plate with drops of a weak, freshly-made solution of potassium ferricyanide; as long as any ferrous salt remains, the mixture turns blue, but as soon as the oxidation is complete no blue colour is produced on mixing the drops. Hydrochloric acid is used to acidify the solution instead of sulphuric acid. In other respects the estimation of ferrous iron by bichromate can be carried out as described under potassium permanganate.

VOLUMETRIC PROCESSES IN WHICH PRECIPITATION OCCURS

The estimation of chlorine (present as chloride), (1) in *neutral* solutions.

10 c.c. of the chloride solution are placed in a white dish and 2 or 3 drops of K_2CrO_4 Aq (5 per cent.) are added.

$\frac{\text{N}}{10} \text{AgNO}_3$ is run in from the burette till the red tint, due to formation of Ag_2CrO_4 , no longer disappears on stirring. Suppose only 7.5 c.c. are required, then the chloride solution is weaker than $\frac{\text{N}}{10}$, and its strength is really

$\frac{7.5}{10} \times \frac{\text{N}}{10}$. It must therefore contain $\frac{7.5}{10} \times 3.55$ gm. of chlorine (as chloride) per litre.

(2) In solutions slightly acidulated by HNO_3 .

Method (1) is now unsuitable, as Ag_2CrO_4 is readily soluble in HNO_3 and will not appear. The following method (Volhard's) is therefore employed:—

(i.) To 10 c.c. of the chloride solution in a white dish (containing about 4 drops of $\text{Fe}_2(\text{SO}_4)_3\text{Aq}$), $\frac{N}{10}\text{AgNO}_3$ is added in excess; (ii.) $\frac{N}{10}\text{AmCNS}$ is now run in till all the surplus Ag is precipitated as AgCNS , as shown by the permanence of the reddish colour due to $\text{Fe}(\text{CNS})_3$. (iii.) Deduct the number of c.c. used in (ii.), say n_2 , from that used in (i.), say n_1 . Then the strength of the chloride solution is $\frac{n_1 - n_2}{10} \times \frac{N}{10}$. It therefore contains $\frac{n_1 - n_2}{10} \times 3.55$ gm. of Cl (as chloride) per litre.

VOLUMETRIC ESTIMATION OF PHOSPHATES.

Reagent.—Solution of uranium acetate or nitrate, standardised so that 20 c.c. = .1 gm. of P_2O_5 or 1 c.c. = .005 gm. of P_2O_5 .

Indicator.—Freshly prepared solution of K_4FeCy_6 (10 per cent.). As soon as excess of uranium salt has been added to the phosphate solution, a drop of the latter added to a drop of the indicator on a white slab, will strike a reddish-brown colour, due to uranium ferrocyanide.

Sodium acetate solution.—The following solution is also required. Dissolve 10 gm. of sodium acetate in about 90 c.c. of distilled water and make up to 100 c.c. with strong acetic acid.

Method.—Place 50 c.c. of urine (or other suitable solution) in a beaker, add 5 c.c. of the sodium acetate solution, and warm the mixture on the water-bath to about 80° . Run in the uranium solution from a burette, stir constantly, and test from time to time on the slab. When the brown colour first appears, warm well, and test again; if the brown still shows, the end point is reached.

Ex. Suppose 17 c.c. have been run in, then 50 c.c. of sample contain $17 \times .005$ gm. of P_2O_5 .

WEIGHTS AND MEASURES

1 lb. Avoirdupois ..	=	16 oz. Av. = 7,000 grains
		= 453·6 gm.
1 oz. Avoirdupois ..	=	437·5 grains = 28·35 gm.
1 lb. Troy ..	=	12 oz. Troy = 5,760 grains.
1 oz. Troy ..	=	480 grains.
1 grain ..	=	64·8 milligrammes.
1 gallon ..	=	8 pints = 4·54 litres.
1 pint ..	=	20 fluid oz. = 568 c.c.
1 fluid oz. ..	=	8 fluid drachms = 28·4 c.c.
1 fluid drachm ..	=	60 minims = 3·55 c.c.
1 minim ..	=	·06 c.c.
1 gallon of water at 62° F. weighs ..	=	70,000 grains, or 10 lb.
1 cubic foot of water	=	997 oz. Av. = 28·3 litres.
1 yard ..	=	·9144 metre.
1 foot ..	=	·3048 metre.
1 inch ..	=	·0254 metre.
1 metre (m.) ..	=	10 decimetres (dm.).
„ „ ..	=	100 centimetres (cm.).
„ „ ..	=	1,000 millimetres (mm.).
„ „ ..	=	39·37 inches.
1 litre ..	=	1,000 cubic centimetres (c.c.).
„ ..	=	1·76 pints.
1 cubic metre ..	=	1,000 litres.
1 kilogramme (kg.) ..	=	1,000 gm.
„ „ ..	=	2·205 lb. Av.
1 gramme ..	=	10 decigrammes (dg.).
„ ..	=	100 centigrammes (cg.).
„ ..	=	1,000 milligrammes (mg.).
„ ..	=	15·432 grains.

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